IODINE FLUORINE CHEMISTRY

A thesis submitted to the
University of Glasgow in fulfilment
of the requirements for the degree of
DOCTOR OF PHILOSOPHY

by

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October 1973

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ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to Dr. J.M. Winfield for his constant encouragement and supervision throughout the course of this work.

My thanks is extended to my postgraduate colleagues and other members of the staff for many informative discussions, and particularly to Dr. C.J.W. Fraser for her assistance with the ^{18}F work. I should also like to acknowledge the assistance of Owen Chambers and John Berry in obtaining some results as part of their 4th year projects.

The award of an S.R.C. Research Studentship is gratefully acknowledged.

ABSTRACT

This thesis describes the preparation, identification and some reactions of substituted derivatives of iodine pentafluoride. Some data on the rate of fluorine exchange between IF_5X (X = OMe or OPh) and Me_3SiF using an ^{18}F radioactive tracer technique has been obtained with a view to future application of this technique to iodine(V) fluorides.

Perfluoroalkyliodides are oxidised to the corresponding perfluoroalkyliodine(V) tetrafluoride by chlorine trifluoride in C_6F_{14} at -78°C. Trifluoromethyliodine(V) tetrafluoride is isolated as a white solid at 20°C and is identified by its ^{19}F n.m.r., i.r. and mass spectra. Evidence for the formation of trifluoromethyliodine(III) difluoride has also been obtained. Other perfluoroalkyl derivatives which have been prepared are $C_2F_5IF_4$, $(CF_3)_2CFIF_4$, $n\text{-}C_4F_9IF_4$ and a mixture $F_4ICF_2CF_2IF_4$ and $F_2ICF_2CF_2IF_2$. These compounds have been identified spectroscopically and in some cases by their elemental analyses.

Oxidation of the compounds, $SF_5(CF_2)_nI$, by chlorine trifluoride yields fluoroalkanes having both $-SF_5$ and IF_4 or $-IF_2$ substituents.

Iodopentafluorobenzene reacts with chlorine trifluoride below room temperature to form pentafluorophenyliodine(V) tetrafluoride, and mass spectral evidence strongly suggests that $C_6F_4(IF_4)_2$ is one of the products from the oxidation of 1, 4-$C_6F_4I_2$ under similar conditions. Bromopentafluorobenzene is not oxidised by ClF_3 but addition of chlorine and fluorine to the ring occurs. Similar behaviour is observed between C_6F_5I and excess ClF_3 or between $C_6F_5IF_4$ and ClF_3.

The stability, with respect to decomposition, of the compounds

R_FIF_4 [R_F = CF_3, C_2F_5, $(CF_3)_2CF$, n - C_4F_9, $SF_5(CF_2)_4$ or C_6F_5] has been investigated. The stability depends to a great extent on the size of the R_F group. CF_3IF_2 decomposes more readily than CF_3IF_4. The products from the decomposition of CF_3IF_4 are CF_4, CF_3I, IF_5, I_2 and possibly IF_3 and a scheme has been proposed to explain the products formed.

In the presence of AsF_5, CF_3IF_4 decomposes at -78°C to give CF_4 and a thermally unstable solid which may be $IF_3 — AsF_5$. CF_3IF_4 and $C_2F_5IF_4$ react with hexafluoropropene to form $(CF_3)_2CFI$. Decomposition products of perfluoroalkyliodine(V) tetrafluorides are also formed.

Alkoxo derivatives of IF_5 and R_FIF_4 are obtained from stoicheiometric reactions of these compounds with Me_3SiOR or $Me_2Si(OR)_2$ (R = Me or Et). IF_4OMe is obtained as a white solid which loses HF slowly at 20°C. Similarly, IF_4OEt, a colourless liquid at 20°C, loses HF on standing. Higher substituted derivatives are similarly prepared. ^{19}F n.m.r. spectra indicate that the disubstituted compounds $IF_3(OMe)_2$, $IF_3(OMe)(OEt)$ and CF_3IF_3OMe undergo redistribution reactions. In particular, CF_3IF_3OMe gives $CF_3IF_2(OMe)_2$ and CF_3IF_4. $I(OMe)_5$ is not isolated pure but is contaminated by $IF(OMe)_4$. These alkoxo iodine(V) fluorides decompose readily at room temperature.

The reactions between IF_5 and some other organosilicon compounds have also been investigated. The reaction of IF_5 with trimethylchlorosilane produces a yellow solid which decomposes below room temperature, giving a variety of products. IF_5 reacts with hexamethylsiloxane, but the desired product, IOF_3, is not isolated. Me_3SiF is produced only slowly in the reactions of IF_5 with $Me_3SiOC_6F_5$ and with a mixture of $Me_3SiOCH(CF_3)_2$ and $Me_3SiOC(CF_3)_2OCH(CF_3)_2$. However, IF_5 reacts vigorously with Me_3SiSMe and Me_3SiNEt_2 below room temperature.

Acetatoiodine(V) fluorides are not isolated in the reactions of IF_5 with $Me_3SiOC(O)R$ (R = CH_3 or CF_3). Instead, free iodine is produced and the acetate groupings are detected as the corresponding methyl esters and as acetyl and trifluoroacetyl fluorides. Silicon-carbon bond cleavage also occurs, Me_2SiF_2 being a major product.

IF_5 reacts with tetramethylsilane and the fluoromethylsilanes, Me_3SiF and Me_2SiF_2, by cleaving the Si-C bonds. Iodine and HF are also produced but no substituted derivative of IF_5 is isolated.

The fluorination of some sulphite and phosphite esters has been studied. IF_5 undergoes substituent-exchange reactions with sulphite esters to yield the corresponding fluorosulphite ester and IF_4OR(R = Me,Et). IF_5 reacts vigorously with $P(OMe)_3$ at -80°C and above, producing a variety of pentavalent phosphorus-fluorine derivatives and iodine.

The reactions of IF_5 with the phenoxo compounds Me_3SiOPh and $(PhO)_2SO$ result in the formation of HF and possibly fluorinated phenyl compounds.

The behaviour of IF_4OMe in several solvents has been investigated and compared with IF_5. IF_4OMe methylates pyridine and slowly fluorinates the C-H bonds of benzene, but is generally a less vigorous fluorinating agent than IF_5.

Some quantitative determinations of the rate of fluorine -18 exchange between Me_3SiF and WF_5X (X = OMe and OPh) have been performed. The rates of exchange are compared and the possible application of this technique to iodine(V) fluorides is discussed.

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INTRODUCTION

The existence of interhalogen compounds has been recognised for well over a hundred years. Those containing fluorine are extremely reactive as fluorinating agents and, in this respect, they are rather similar to elemental fluorine. The high reactivity and attendant difficulties in handling halogen fluorides delayed a thorough investigation of their chemistry for many years. The demands of the nuclear programme and, more recently, the search for efficient rocket fuel oxidants have provided the impetus for a systematic study into these and other fluorine compounds.

All interhalogens can be prepared by direct union of the elements. By varying reaction conditions, a particular compound is preferentially formed when alternative combinations are possible. Thus, ClF results when equimolar proportions of the two elements are passed through a Nickel tube at 250°C. With a higher proportion of fluorine, combination will give the trifluoride, while the pentafluoride is obtained only by using a large excess of fluorine at 350°C and a pressure of 250 atmospheres[1]. The bromine fluorides are similarly prepared, except that the pentafluoride is easier to obtain than ClF_5, in keeping with the more basic character of the heavier halogen. BrF_7 and ClF_7 are unknown.

Iodine forms compounds in the -1, +1, +3, +5 and +7 oxidation states. Iodine fluorides have been reported for the positive oxidation states. - Fluorine is the most electronegative of the elements and its high ionization potential makes the existence of even solvated cationic species unlikely. - The average bond energies of the halogen fluorides are expected to increase with increasing polarity of the bond (electronegativity difference between the heavier halogen atom and fluorine) and to decrease with the number of ligands in a series, such as IF, IF_3, IF_5, IF_7. In general this behaviour is observed.

For example:[1]

Compound	Average bond energy ($K\ cal\ mol^{-1}$)	$\Delta G^{o}_{f298^{o}K}$ (free energy of formation at 298K ($K\ cal\ mol^{-1}$)
IF	67	-28.1
IF_3	(-65)	*
IF_5	64	-183.2
IF_7	55.2	-200.5

*estimated from bond energies of other halogen fluorides.

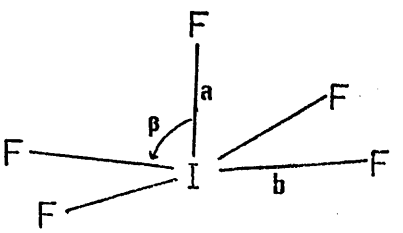
At normal temperatures both IF and IF_3 are unstable with respect to disproportionation to IF_5 and I_2, but at high temperatures IF_5 may be expected to dissociate directly to lower fluorides and atomic fluorine. IF_7 dissociates to IF_5 and fluorine above $450^{o}C$[2].

The structures of the halogen fluorides are of considerable interest because the molecules possess lone pairs which are stereochemically active. Thus far, no measurements of i.r., Raman, or n.m.r. spectra of IF have been published. Cole and Eleverum[3] estimate the bond length to be $1.906A^{o}$. It seems reasonable to propose that the I - F bond has considerable ionic character and a high degree of association in condensed states. Both ClF_3 and BrF_3 are T-shaped molecules in the gas phase[1]. The structures are derived from a trigonal bipyramid with two pairs of electrons occupying equatorial sites. IF_3 is most likely to have this planar T-shaped structure (C_{2v}). Again, some degree of association in the condensed states is expected and has been proposed[4].

The pentafluorides of chlorine, bromine and iodine all have structures based on a square pyramid with fluorine at the apices and the heavier halogen atom somewhat below the basal plane containing four fluorine atoms, the lone pair occupying the remaining octahedral site (Fig. I1). Begun, Fletcher and Smith[5] report the infrared and Raman spectra of all three pentafluorides, giving

assignments of the fundamental frequencies on the basis of C_{4v} symmetry. For these assignments, discrete molecular species are assumed present in both liquid and gas phases. More recently, however, Selig and Holzman[6], and Alexander and Beattie[7] report a narrowing and simplification of the Raman spectrum in going from solid to liquid to gas. In particular, the 697cm^{-1} band (Table 4 Ch.1) gradually disappears leaving, at 130°, only a single peak at 703cm^{-1}. It is proposed by Selig and Holzman that the additional band in the 700cm^{-1} region is due to polymerization. On the other hand, Alexander and Beattie suggest that the splitting of the highest frequency band in the Raman results from the presence of two "site" symmetries in the liquid. Although the actual reason for this phenomenon is uncertain, "association", found in condensed phases, appears to be responsible.

The ^{19}Fn.m.r. spectrum of liquid IF_5, consistent with square pyramidal C_{4v} symmetry, shows a 1:1 doublet (δ = +10.9) and a quint-uplet (δ = +59.7) with components of intensities 1:4:6:4:1. (Chemical shifts downfield relative to CCl_3F). The above "association" in the liquid does not significantly perturb the bond angle or electronic configuration of the molecule. Recent microwave studies by Bradley, Brier, and Whittle[8] give rotational constants for IF_5 and confirm that the molecule has C_{4v} symmetry in the gas phase. These rotational constants together with electron diffraction data[9] enable the structure of IF_5 to be evaluated:



a = 1·844 A°
b = 1·869 A°
β = 81·9°

Fig.I.1

The ^{19}Fn.m.r. spectrum of liquid IF_7 gives rise to a broad symmetric doublet, interpreted as partially collapsed and unresolved $^{19}F - ^{127}I$ coupling,[10] but no detailed structural information has been determined from its n.m.r. spectrum. A crystal study by Burbank[11] suggests that the structure of IF_7 is related to the pentafluoride with the lone pair below the four basal fluorines being replaced with two fluorine atoms. However, recent vibrational spectroscopic data[12] on IF_7 has been interpreted in terms of a non-rigid D_{5h}, structure based on a pentagonal bipyramid.

Two bonding theories have been employed to explain the structures of the halogen fluorides: (a) valence bond theory; (b) molecular orbital theory. In its valence shell iodine has the electronic structure $(5s)^2(5p)^5$. In iodine fluorides and in polyhalides generally, the number of bonds formed exceeds the number of electrons with free spin. In a localised co.valent bond interpretation the most obvious way to account for the increase in covalency is to suppose d(or f) orbitals participate in the bond formation. The C_{4v} structure of IF_5 can then be explained by assuming the central atom uses a set of sp^3d^2, octahedral hybrid orbitals, with one orbital containing an unshared pair of electrons. The bond angles of less than 90^o are assumed to result from the fact that lone pair-bond pair repulsions exceed bond pair-bond pair repulsions[13]. This concept is unsatisfactory in that it requires promotion of two electrons to d orbitals of high energy. Also, n.q.r.[14] and Moessbauer[15] studies suggest the bonds in IF_5 do not have appreciable s character.

The M.O. treatment of the bonding is based on two main ideas: (1) the use of outer d orbitals is so slight they may be neglected and (2) the bond angles close to 90° and 180° suggest that orbitals perpendicular to one another, namely p orbitals, are being used. In this concept, IF_5 is postulated to have two 3 centre - 4 electron bonds and one 2 centre - 2 electron bond, with the lone pair in an s orbital[16]. The 3 centre - 4 electron bond is formed from a 5p orbital of iodine and σ orbitals from the two fluorine atoms. Presumably, the fluorine orbital is some sort of sp hybrid. Of the four electrons populating this molecular orbital only two are bonding. The two non-bonding electrons are expected to reside completely on the more electronegative fluorine atoms, thus making the I-F equatorial bonds quite polar. Hence, these bonds should be weaker and longer than the 2 centre-2 electron I-F axial bond, agreeing with experiment. By use of a modified Hückel theory on a linear combination of atomic p orbitals, Wiebenga and Kracht[17] predict square pyramidal geometry for IF_5 but a more recent treatment, applying I.N.D.O. and C.N.D.O./2 theories to the geometry and bonding of interhalogens, predicts a trigonal bipyramidal structure for IF_5 to be more stable than a square pyramidal structure by some 5-9eV[18]. It appears that predictions of the geometry of these interhalogens on the basis of theoretical treatments depend on the assumptions and approximations made in the calculations. In general terms, the p - σ-model described above allows quite accurate investigations of the effect of environment on molecular geometry but the model has only limited power to predict those properties which depend on charge distribution[19]. This inadequacy points to the fact that interactions between non-bonding valence electrons of the bonded atoms cannot be neglected. Also, by including d orbitals in the

calculations a more accurate picture of the bonding may be obtained.

Iodine pentafluoride is the best characterised and most easily prepared of the iodine fluorides. It is readily formed by direct combination of the elements at room temperature. It is a colourless liquid at room temperature; m.pt.9.43°C, b.pt.100.5°C. The thermodynamic properties have been investigated by Osborne, Schreiner and Selig[20] and they note that the heat capacity of liquid IF_5 is large compared with the extrapolated heat capacity of the solid. This effect is thought to be suggestive of associative effects in the liquid phase. The compound was earlier recognised as an associating liquid by Rogers[21], who supported his viewpoint with evidence including a high value for Trouton's constant, viscosity and surface tension data and an abnormal value for the correlation factor for the dielectric constant of the liquid. The high dielectric constant for IF_5 of 36.14[16] should enable the liquid to function as a good ionizing solvent. The specific conductivity of IF_5, 5.4×10^{-6} $ohm^{-1}cm^{-1}$[1], indicates self-ionization, probably of the form:

$$2IF_5 \rightleftharpoons IF_4^+ + IF_6^-$$

It should be noted at this stage that the literature values may be quite inaccurate in view of the possibility of hydrolysis by traces of water.

In comparison to other halogen fluorides, IF_5 is a mild fluorinating reagent with slight oxidising powers, a tentative order of decreasing reactivity being

$$ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5 > BrF$$[1]

Glass is attacked rapidly by IF_5 at elevated temperatures, and even metals of low reactivity, such as Cu and Ni, are partially fluorinated. It reacts vigorously with H_2O, sometimes violently, but without liberating oxygen[22]. In the early 1900's, Moissan described the

action of IF_5 on many elements and compounds[23]. Arsenic, antimony and boron inflame on contact with the liquid; molybdenum and tungsten inflame when heated; alkali metals react violently when heated; silver, magnesium, iron and chromium are attacked only slightly by the reagent. Phosphorus burns in IF_5 forming PF_3. Similarly, Tullock and his co-workers[24] find that the chief product from the reaction of sulphur and IF_5 is SF_4. Since it is a milder reagent than other halogen fluorides, IF_5 has been used extensively in the fluorination of organic compounds[25]. Compounds rich in hydrogen inflame in the pentafluoride at room temperature. Hydrogen itself does not react perceptibly at 100°C. Organic halides often react smoothly. A mixture of IF_5 and iodoform reacts at 80°C to give CHF_3 and CHF_2I in the approximate ratio of 15:1.

IF_5 forms both ionic and molecular complexes. Products formulated as $IF_4^+.SbF_6^-$ and $K^+IF_6^-$, which on mixing give IF_5 and $KSbF_6$, have been isolated[1]. $NOIF_6$ has been obtained by direct combination of NOF and IF_5[26]. Clifford, Beachell and Jack[27] have studied the acid properties of IF_5 in anhydrous hydrogen fluoride solution and they consider fluoroiodic acid, formulated as $H_2F^+.IF_6^-$, to have approximately the same strength as anhydrous fluoroacids of Nb(V), Ta(IV), Ge(IV) and Ta(IV). Metals and metal fluorides added to the acid form a variety of complex salts. The following are reported to be formed by BaF_2, NaF and AgF, respectively, in IF_5-HF solution, $Ba(IF_6)_2$, $BaF.IF_6$, $BaHF_3$; $NaIF_6$, $NaHF_2$; $AgIF_6$. CsF reacts with IF_5 to form both 1:1 and 1:3 adducts[28]. The 1:3 adduct $CsF.3IF_5$ can be pyrolyzed at 90°C to give the 1:1 adduct, formulated as $Cs^+IF_6^-$. No evidence for the formation of a distinct 1:2 complex can be obtained. The structure of IF_6^- has not been unambiguously defined but it would appear to have a symmetry of C_{2v}[29], or lower[28]; the lone

pair is again stereochemically active. Analysis of the Raman spectrum of $IF_4^+.SbF_6^-$ [30] suggests that the IF_4^+ ion is trigonal bipyramidal (C_{2v}) with two fluorine atoms in axial positions, the other fluorine atoms and the lone pair of electrons being at the corners of the triangular equatorial plane.

Molecular complexes of iodine pentafluoride with several organic bases have been reported. A stable crystalline 1:1 adduct is formed with dioxan[31]. Similarly, pyridine and dimethyl formamide form stable 1:1 complexes in IF_5 solutions. Aynsley, Nichols and Robinson[32] find that the pentafluoride forms molecular complexes with several oxides and oxy-acid salts; for example $NO_2.IF_5$, $WO_3.2IF_5$, $2MoO_3.3IF_5$, $Ba(NO_3)_2.IF_5$, and $KIO_4.IF_5$. Results indicate that the complex formed between XeF_4 and IF_5 in solution is essentially molecular[33]. Complexes of IF_5 with XeF_2 of stoicheiometries 1:1[34] and 1:2[35] are reported to be molecular. In particular, the crystal structure of the molecular adduct $XeF_2.IF_5$(m.pt.98°C)[36] establishes the existence of discrete XeF_2 (linear) and IF_5 (square pyramidal) entities.

Iodine monofluoride has not been isolated as a pure substance at room temperature, since it disproportionates rapidly:

$$5IF \longrightarrow 2I_2 + IF_5 .$$

Durie[37] has observed the emission spectrum of IF(4350-6900A°) in the bright, greenish yellow flame produced by the reaction of fluorine with iodine crystals. Iodine monofluoride is formed in the reaction of silver fluoride with iodine at -10° to -30°C[38] but is more readily prepared by the reaction of fluorine with iodine in CCl_3F at -45°C[39]. Addition compounds of iodine monofluoride have been reported: L_mIF (L = 2.2[1] bipyridyl[1], quinoline, pyridine; m = 1,2). The action of IF on CsF produces Cs_3IF_6 and I_2. No complex of the type $CsIF_2$

can be isolated. With CsCl, IF forms $CsIF_4$ and $CsICl_2$. A mixture of IF_5 and I_2 adds I-F across olefinic double bonds. It is proposed that IF, formed in the equilibrium

$$IF_5 + 2I_2 \rightleftharpoons IF,$$

is the species which participates in the reaction[40], although the mechanism has not been established.

Iodine trifluoride can be prepared by passing fluorine diluted with nitrogen through a solution of iodine in CCl_3F at -78°C[4]. The initial product, a suspension of brown IF, turns yellow as it is converted to the trifluoride. Schmeisser and Naumann[41], using differential thermal analysis methods, have shown that IF_3 decomposes into I_2 and IF at -12°C. Similar to IF, iodine trifluoride reacts with nitrogen bases(L) to give complexes of the type $IF_3.L$[4,42]. $IF_3.2py$(py = pyridine), formed when IF_3 is reacted with pyridine in 1:2 mole ratio, has been formulated as $[IF_2py_2]^+.[IF_4]^-$. NOF reacts with IF_3 in CCl_3F forming $NOIF_4$. Tetrafluoroiodates, MIF_4(M = K, Rb, Cs), first prepared by Hargreaves and Peacock[43], who reacted MI with iodine pentafluoride at room temperature, can also be formed directly from IF_3 and CsF[4]. Iodine trifluoride also forms adducts with Lewis acids. Colourless $IF_3.AsF_5$, formulated as $IF_2^+ AsF_6^-$, is reported to decompose above -22°C to a blue green solid[4].

The heptafluoride of iodine is a colourless gas at room temperature and a white solid at 0°C. The solid sublimes at 4.77°C and melts under its own vapour pressure, forming a colourless liquid at 6.45°C(triple point)[1]. It can be prepared directly from the elements, but IOF_5 is frequently present as an impurity. Bartlett and Levchuk[44] recommend that the heptafluoride is best prepared from metal iodides, such as PdI_2, since elemental iodine is difficult to dry.

IF_7 is a stronger fluorinating agent than IF_5 and its reactions with many substances have been qualitatively described by Ruff and Keim[45]. Attempts to increase the co-ordination number of iodine from seven to eight by preparing compounds of the type MIF_8 (M = Na, K,Rb) from IF_7 and the corresponding alkali metal fluoride have proved unsuccessful[46]. IF_7 forms colourless solids with BF_3, AsF_5 and SbF_5 of constitution $IF_7.BF_3$, $IF_7.AsF_5$ and $IF_7.3SbF_5$ respectively[47]. $IF_7.AsF_5$ has been shown to contain the octahedral IF_6^+ ion[48]. Although no stable molecular complexes of IF_7 have been isolated, IF_7 forms coloured solutions in organic n and σ donor solvents[49], indicating weak, charge-transfer complexes are formed in solution.

Polyvalent iodine fluorides, where one or more of the fluorine atoms is replaced by another ligand, have been reported. These derivatives are of four main types: (1) an oxygen atom replaces two fluorine atoms forming iodine oxyfluorides; (2) one fluorine atom is replaced by an oxygen donor, for example the trifluoroacetate group; (3) an organic group is bonded to iodine <u>via</u> a C-I bond; (4) a fluorine atom is replaced by another halogen. There is considerable similarity between iodine fluorides and compounds with both fluorine and oxygen bonded to iodine. This similarity also exists among the other halogen fluorides. No oxyfluoride derivatives of I(III) have been reported, demonstrating the ability of both fluorine and oxygen to promote high valency states in other elements. Several oxyfluorides of I(V) and I(VII) have been described[50]. IO_2F is conveniently prepared by the action of fluorine on a solution of iodic acid (HIO_3) in anhydrous liquid HF. $[IO_2^+][AsF_6^-]$ can be isolated from the reaction of IO_2F and AsF_5 in anhydrous HF. Conversely, IO_2F is able to accept a fluoride ion. Investigation of the structure of KIO_2F_2 showed the presence of $IO_2F_2^-$ groups.

Oxyfluorides are very similar to their corresponding iodine fluorides in that they have the ability to both donate and accept fluoride ions. IOF_3 is prepared from the reaction of diiodine pentoxide (I_2O_5) with boiling IF_5[32]. Iodyl fluoride is obtained from IOF_3 at 100°. On this basis, IOF_3 has been formulated as $IO_2F.IF_5$. However, a crystal structure of white crystalline IOF_3 shows that it has a molecular configuration similar to $IO_2F_2^-$[51], the molecule being a trigonal bipyramid distorted due to the influence of the non bonding electrons.

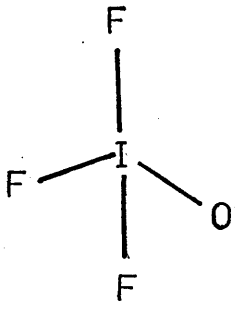


Fig. I.2.

Many intermolecular I...F contacts are considerably less than the sum of the van der Waals radii, indicating the likelihood of strong intermolecular interactions. It must be noted that oxygen and fluorine atoms are not readily distinguished by X-Rays and consequently there must still be some doubt about the structures of both $IO_2F_2^-$ and IOF_3. The oxyfluorides of I(VII) are not well characterised. Only in the case of IOF_5 have their structures been thoroughly investigated by spectroscopic methods. IOF_5 is produced when the heptafluoride reacts with silica or small amounts of moisture. Its ^{19}F n.m.r.[10] shows four equivalent and one unique fluorine atom[5](Fig.I.3), consistent with C_{4v} symmetry and in agreement with the vibrational[52] and microwave[53] spectroscopic interpretations.

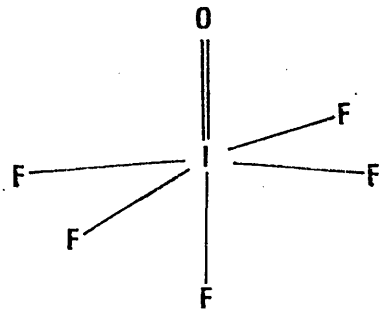


Fig.I.3.

Analogous to IO_2F, IO_3F is prepared by fluorinating meta- or ortho-periodic acid, with elemental fluorine, in anhydrous HF. Periodyl fluoride also acts as a weak base in anhydrous HF. $HOIOF_4$, tetrafluoroorthoperiodic acid, is formed when $Ba_3H_4(IO_6)_2$ is allowed to react with a 20-fold excess of fluorosulphuric acid[54]. Addition of sulphur trioxide to $HOIOF_4$ gives IO_2F_3. The chemistry of these latter two oxyfluorides has not been investigated in any great detail.

Substituted derivatives of iodine fluorides, where one fluorine atom is replaced by an oxygen ligand are known for both the I(V) and the I(III) oxidation states. No such derivatives have as yet been recorded for I in the +7 oxidation state. Fluorine fluorosulphate oxidises elemental iodine to iodine trifluoride bisfluorosulphonate, $IF_3(SO_3F)_2$, which has been characterised by elemental analysis and ^{19}F n.m.r.[55]. The salt $N(R)_4[IF_4(OC(O)CF_3)_2]$ (R = Me,Et) is reported to form when trifluoroacetic anhydride reacts with $N(R)_4IF_6$[56]. The compound is characterised by i.r. bands at 480, 825, and 570cm^{-1}, assigned to an IF_4 group. However, the characterisation of this compound is not complete as it decomposes to $N(R)_4IO_2F_2$, CF_3OF and I_2. Trifluoroacetate derivatives of I(III) can be isolated at low temperatures. $I(OC(O)CF_3)_3$ is isolated from the reaction of IF_3 with trifluoroacetic anhydride[57]. Similar treatment of Cs_3IF_6 leads to the isolation of species of the type $Cs_3IF_{6-n}(OC(O)CF_3)(n=2,4)$[58]. These derivatives can only be isolated at low temperature and, therefore have not been fully characterised. During their thermal decomposition $(CF_3CO)_2O$ is identified.

Many examples of the isolation of organic derivatives of I(III) and I(V) fluorides are recorded. The action of aqueous HF on (a) iodoso and (b) iodoxy[59] aryl compounds is reported to give the corresponding difluorides as isolable solids.

(a) $ArIO + 2HF \longrightarrow ArIF_2 + H_2O$

(b) $ArIO_2 + 2HF \longrightarrow ArIOF_2 + H_2O$

In view of the reactivity of iodine fluorides, and covalent binary fluorides in general, towards H_2O, it is surprising that these compounds can be isolated. SF_4 reacts with RIO (R = C_2F_5, aryl), under anhydrous conditions to produce the corresponding difluoride at -20°C[60]. Heating SF_4 and $PhIO_2$ for several hours, at temperatures 70°-150°C, produces the corresponding tetrafluoride, $PhIF_4$[61]. SF_4 also replaces acetate ligands by F in compounds of the type $RI(OC(O)CF_3)_2$, (R = alkyl, aryl) to give the corresponding difluorides, RIF_2. Other routes for the formation of alkyl and aryl di-and tetra-fluorides involve oxidative fluorination of the corresponding iodide. Elementary fluorine will oxidise CF_3I[62] and C_6F_5I[63]. to the corresponding iodine (III) difluorides under mild conditions.

$$R_FI + F_2 \longrightarrow R_FIF_2 \quad [R_F = CF_3,\ C_6F_5]$$

The instability of these compounds - they decompose below 0°C - makes a thorough investigation of their properties difficult. Rondestvedt[64] has found it more convenient to use excess R_FI(R_F = C_2F_5,C_3F_7,C_4F_9, C_6F_{13}, $C_{10}F_{21}$) and ClF_3 in perfluorohexane solvent to produce the iodine (III) difluoride

$$3R_FI + 2ClF_3 \longrightarrow 3R_FIF_2 + Cl_2$$

The corresponding tetrafluorides can then be produced by using excess ClF_3

$$3R_FI + 4ClF_3 \longrightarrow 3R_FIF_4 + 2Cl_2.$$

The pure tetrafluorides can also be obtained using BrF_3 and BrF_5 in slight excess. Some perfluoroalkyl iodine (III)difluorides and iodine (V) tetrafluorides prepared by their method have been investigated and their properties will be mentioned in Chapter One.

The ternary interhalogens IF_2Cl and $IFCl_2$ have been reported by Schmeisser and his co-workers[65]. Attempts to prepare interhalogens, containing four different halogen atoms, by the action of BrCl on IF

at -78°C in CCl_3F, yield a yellow brown solid of composition IFCl, formulated as IF_2^+ ICl_2^-. No stable compounds containing iodine, bromine and fluorine have been isolated. Reaction of IF_2Cl with $AgNO_3$ produces IF_2NO_3, which is stabilized by complexing with pyridine. These derivatives IF_3 are stable only at low temperatures. Their properties have, therefore, not been extensively studies. Meinert and Klamm[56] state that colorimetric and conductimetric titrations of $(Et)_4NIF_6$ and $(Et)_4NCl$ in acetonitrile indicate formation of the anion $IF_4Cl_2^-$ and that IF_5 with XCl(X = I, ICl_2, Br, Cl) in $CF_2ClCFCl_2$ react in pyridine (py.) to give an adduct which may be formulated as $X(py)_2^+$ IF_5Cl^-[66]. The ternary I(V) interhalogen, IF_4Cl is assumed to be an intermediate in these reactions. The failure to isolate and characterise this compound is attributed to reaction with the glass container, but attempts by Christe[28] to duplicate the reaction of CsCl and IF_5, reported by Klamm and Meinert to form IF_4Cl, in a metal-Teflon system proved unsuccessful. Cl_2 was isolated.

In the work to be described in this thesis extensive use was made of several spectroscopic techniques to identify and characterise reaction products. The identification of compounds and chemical groupings in molecules by both infrared and Raman spectroscopic methods is well documented. Although information from infrared and Raman spectra does not provide complete certainty concerning the presence or absence of certain groupings, the indications obtained aid structural determinations by other techniques.

Considerable dependence has been put on ^{19}Fn.m.r. spectroscopy for the characterisation of compounds during this investigation. Fluorine-19 is the only naturally occuring isotope of the element. The magnetic moment of ^{19}F is only slightly smaller than that of ^1H so its sensitivity is relatively high. It has a nuclear spin of $\frac{1}{2}$ and, therefore,

experiences no complications from quadrupole relaxations. By virtue of the large values of ^{19}F chemical shifts and spin coupling constants it is often possible to obtain much information about molecular structures and molecular dynamic processes. However, the theoretical treatment of the origin of ^{19}F chemical shifts and coupling constants is not well developed. According to the theory of Saika and Slichter[67] variations in the local paramagnetic circulations of the fluorine atom are the dominant cause of chemical shifts in fluorine compounds. The paramagnetic contribution, which represents a shift to low field (deshielded) is greatest in covalently bonded fluorine and zero in the spherically symmetrical F^- ion. The magnitude of the paramagnetic contribution may thus expect to depend on the amount of ionic character in the chemical bond. Therefore, a simple correlation of chemical shift with electronegativity of the group bonded to F is expected. Other factors which influence chemical shift, attributed to both bulky group dispersion forces and to the presence of double bond character can be accounted for in terms of the presence of low lying electronic energy levels in the molecule[68]. ^{19}F spin-spin coupling is not solely controlled by the Fermi contact term but dipole effects are also thought to make a significant contribution.

Although fluorine has no nuclear quadrupole moment, iodine ^{127}I with spin 5/2 does possess a nuclear quadrupole moment. As the rate of quadrupolar relaxation of iodine in IF_5 is large compared with coupling between iodine and fluorine the spectrum shows no evidence of ^{127}I - ^{19}F coupling but in IF_7, where the I-F coupling is large [10], the ^{19}F spectrum is broadened.

The third spectroscopic technique used in this study was mass spectrometry. During the development of mass spectrometry,

investigation of inorganic compounds assumed secondary importance to the design and improvement of analytical methods for organic materials. The mass spectrometer has been extensively employed in elucidating composition and structure of complex mixtures of hydrocarbons, particularly in the petroleum industry. More recently, these methods have been applied to multicomponent mixtures of fluorocarbons. Since thermochemical studies of fluorine compounds are very difficult, the electron impact method is also most important in studying the strength of bonds in compounds containing fluorine. The electron impact process gives rise to both positive and negative ions but the formation of a negative ion is less probably by a factor of about 10^{-2}. Therefore, positive ion mass spectrometry is the more popular of the two alternative techniques. Theoretical considerations show that the ionisation process in mass spectrometry is not simply the removal of an electron from a single bond in a molecule[69]. The redistribution of electronic charge between the bonds takes place so rapidly that all the bonds are weakened simultaneously, but there will often be a bond which is weakened much more than others and bond ionisation can be interpreted in that sense. For large polyatomic molecules, it is thought that there is a mechanism whereby the "weak point" can "wander about" in the molecule dissociation occurring when the electronic configuration enables it to take place most easily[69]. Although the stability of the fragments, both charged and uncharged, which are formed in a fragmentation process may often play an important role in determining the mode of fragmentation[69], the major fragments in mass spectra are best rationalised by bearing in mind that the most stable ion products are those which are formed by the most favourable reaction pathways[70]. Certain modes of fragmentation are confirmed by the observation in the mass spectrum of metastable

peaks. These are usually weak diffuse signals and often appear in the mass spectrum at non-integral masses. How these peaks arise is well understood and will be discussed later. The advantage of this technique with compounds of low stability, like those described in this study is that, although molecular ion peaks are not often observed, the breakdown patterns are generally characteristic of the product. The conditions of temperature, pressure and sampling under which the spectrum was run could be varied to obtain optimum results.

Fluorine has a number of radio-active nuclides of which ^{18}F has the longest half-life, 110 mins[71]. This half-life is relatively short in comparison with other nuclides which are used as radio-active tracers, and effectively limits the period over which tracer experiments may be carried out. However, a fluorine-18 tracer technique has been employed to study exchange of substituted tungsten hexafluorides with Me_3SiF[72]. It was hoped to use this technique to study exchange in substituted derivatives of iodine fluorides, but an investigation of more stable tungsten hexafluoride derivatives preceded this and did not allow enough time to extend the technique to iodine fluoride derivatives.

The physical and spectroscopic properties of IF_5 have been investigated, so that general agreement has been reached on some empirical observations, but interpretation of these observations in terms of the geometry and electronic properties of the molecule has been lacking. Although IF_5 is the least reactive of these more stable halogen fluorides, the reported substituted derivatives of IF_5, which are stable at normal temperatures, are few in number. It was hoped in this work to devise methods of preparing stable substituted derivatives of IF_5 and that a study of their preparation and properties would lead to a better understanding of the factors affecting the reactivity of

IF_5 and its derivatives. These derivatives should provide model systems for investigating the chemical and physical properties of iodine in a high oxidation state; for example, the nature of the iodine-ligand interactions and the mechanism of substitution reactions. Necessary for a study of this type is a knowledge of the co-ordination number at, and the distribution of ligands around the iodine. The information obtained could hopefully be applicable to a study of high oxidation state fluorides of elements generally.

GENERAL EXPERIMENTAL METHODS

Standard vacuum techniques were employed throughout, and rigorous precautions were taken to exclude moisture from all systems. A vacuum line was constructed from Pyrex-glass. Standard ground glass joints were greased with Apiezon, Edwards High Vacuum Silicone or Voltalef KelF greases or waxed with Kel-F wax(3M), breakseals and P.T.F.E./ glass stopcocks (Fischer and Porter, Quickfit "Rotaflo", Ace Glass Inc., or West Glass Corp.) were used where required. All glassware was "flamed out" before use. A rotary oil pump and mercury diffusion pump, in series, provided a vacuum of 10^{-4} mm Hg, or better. Involatile compounds were handled in a conventional dry-box using P_2O_5 as dessicant, or in a Lintott inert atmosphere box in which the concentrations of H_2O and O_2 were $\leqslant 10$ p.p.m.

Reactions were generally performed in pyrex vessels fitted with P.T.F.E./glass stopcocks or, in a few cases, breakseals. Attached to these reactions vessels were n.m.r. and sample tubes when required for involatile products .

N.m.r. spectra were recorded using P.E. R.I.O. and Jeol C60-HL instruments with probe temperatures of 33°C and 21°C, respectively at 60MHz for ^1H and 564 MHz for ^{19}F nuclei. ^1H chemical shifts are referred to Me_4Si and ^{19}F chemical shifts are referred to CCl_3F. Chemical shifts are reported as δ values which are positive to low field of reference, unless otherwise stated.

Infrared spectra of gases were recorded in a 5-cm. gas cell fitted with KBr windows and pressures were measured using a mercury manometer. Liquid spectra were recorded as films on AgCl plates and solid spectra were obtained as nujol or fluorolube mulls on AgCl plates. The spectra were obtained using a P.E. 457 instrument.

Laser Raman spectra were obtained as solids or in solution using a Spex Ramalog instrument.

Mass spectra were recorded at 70, 20 or 12 eV. using an G.E.C./A.E.I. MS12 instrument, samples being introduced directly or *via* the gas inlet as appropriate. Mass measurements were performed on a G.E.C./A.E.I. M.S. 902 mass spectrometer.

Elemental Analyses were performed by Bernhardt or in Microanalysis laboratory at Strathclyde University. Sometimes iodine was determined volumetrically.

CHAPTER ONE

PREPARATION AND PROPERTIES OF SOME PERFLUOROALKYL AND ARYL IODINE (V) TETRAFLUORIDES.

INTRODUCTION

Organic compounds containing iodine in its various oxidation states are well characterised [59]. Where the oxidation of the iodine is not ± 1, most of the known, stable compounds have iodine bonded to an aromatic ligand. Examples of compounds in the various oxidation states are:-

I	(-I)	CH_3I
I	(I)	CF_3I
I	(III)	(a) Ar IX_2 (X = Cl, OC(O)R)
		(b) Ar IO
		(c) $(Ar)_2\ I^+\ X^-$
I	(V)	Ar IO_2 (Ar = C_6H_5)

No organic derivatives of I(VII) have been reported. Very few aliphatic representatives have been recorded. CH_3ICl_2 decomposes at -30^oC to CH_3Cl, CH_3I and ICl [73]. Stable chlorovinyl iodine (III) dichlorides [74] have been obtained, suggesting that unsaturation stabilises positive oxidation states of iodine. The stability of α-iodosulfone dichlorides Ar SO_2 CH_2ICl_2 attributed to steric and inductive retardation of S_N1 and S_N2 mechanisms of decomposition [75].

The preparation of aryl iodine (III) difluorides and aryl iodine (V) oxodifluorides, using HF as a fluorinating agent, has been previously described. Little is known of the properties of these compounds. A mixture of C_6H_5IO and 40% HF containing KHF_2 in chloroform, results in a solution of iodobenzene difluoride which can be then used directly as a mild fluorinating agent. Ar IF_2 (Ar = Ph, p-ClPh, p-tolyl, NO_2Ph),

prepared from the action of HgO and HF on the corresponding aryl iodine (III) dichloride [76] is used "in situ " to fluorinate ethylenes

$$PhC = CH_2 \xrightarrow{Ar\ IF_2} PhCF_2 - CH_2Ph .$$

It has been clearly established both in this work and by Rondestvedt [64], that the fluorine bound to iodine in R_FIF_2 and R_FIF_4 is readily liberated by hydrolysis. The hydrolysis product is formulated as $(R_F)_2 I^+ X^-$ (X = OH, IO_3, I, F etc.), an iodonium salt [64]. On the basis of this information, the compounds formulated as $Ar\ IF_2$ in aqueous HF may, in fact, be corresponding iodonium salts, $(Ar)_2\ I^+\ X^-$, in which X^- is of the form IF_4^-. The fluorination of iodine bonded to both oxygen and an organic ligand, using SF_4 to replace the oxygen ligand with fluorine, has also been described. For example, under anhydr ous conditions, the action of SF_4 on $PhIO_2$ produces a white crystalline solid, $PhIF_4$, which can oxidise Ph_3P to Ph_3PF_2 [61].

An alternate procedure for preparing aryl iodine (III) difluorides involves electrolytic oxidation of iodobenzene [77]. A good yield of $PhIF_2$ is reported from the electrolysis of an acetonitrile solution of Ag(I)F and iodobenzene using Pt electrodes.

$$C_6 H_5 I + 2F^- \longrightarrow C_6 H_5 IF_2 + 2e^-$$

The oxidation of elemental iodine by fluorine provides a facile and economical means of preparing IF_5, and many other preparative methods have been described using binary fluorides as oxidative fluorinating agents. The pentafluoride is formed in reactions of I_2 with ClF_3, BrF_3 and RuF_5 [1]. It seems reasonable, therefore, that by controlled oxidative fluorination of alkyl and aryl iodides, monosubstituted derivatives of I(III) and I(V) fluorides should be accessible. Elementary fluorine oxidises CF_3I [62] and C_6F_5I [63] in CCl_3F at low temperatures to the corresponding iodine (III) difluorides, CF_3IF_2 and $C_6F_5IF_2$. Although

little is known concerning these compounds, they have been observed as white or pale yellow solids which decompose below 0°C. In particular, the products formed in the decomposition of CF_3IF_2 are CF_3I, CF_4, IF_5 and I_2. Products formed by the action of fluorine on a solution of perfluoroalkyl iodides are active in promoting low temperature telomerization of tetrafluoroethylene with perfluoroalkyl iodides. This discovery prompted an intensive study of the preparation and properties of these products [64]. In particular, the reaction product from perfluoro-n-butyl iodide in perfluorohexane, as solvent, is perfluorobutyl iodine (III) difluoride contaminated with varying amounts of the I(V) derivative, perfluorobutyl iodine (V) tetrafluoride, and a solid, bis (perfluorobutyl) iodonium hexafluoroiodate.

$$C_4F_9I \xrightarrow{F_2} C_4F_9IF_2 + C_4F_9IF_4 + (C_4F_9)_2 I^+IF_6^-$$

Chlorine and bromine trifluorides and bromine pentafluoride are active fluorinators of perfluoroalkyl iodides, but IF_5 is ineffective. ClF_3 converts a perfluoroalkyl iodide to the iodine (III) difluoride quantitatively, chlorine being the by-product. Larger amounts of ClF_3 yield the iodine (V) tetrafluoride and chlorine. Although bromine fluorides are much less reactive than ClF_3 towards other substrates, it is not possible to prepare pure alkyl iodine (III) difluorides using bromine fluorides. With excess iodide, either bromine fluoride yields a roughly equimolar mixture of di-and tetrafluorides. An unstable dimeric intermediate, containing bromine, which disproportionates to form the di-and tetrafluorides is proposed. It is reported that reactions involving liquid ClF_3 can be controlled at low temperatures (-70 to -50°C) by using large amounts of solvent or excess iodide to prepare the difluorides and perfluorohexane for the tetrafluorides. On addition of ClF_3 vapour, however, the reaction can only be controlled at low

temperatures with constant attention, as occasionally explosions occur [64].

Rondestvedt finds that the difluorides are more stable with respect to decomposition than the tetrafluorides, but that the difluorides are more active telomerization agents. This stability towards decomposition increases with increasing organic chain length. Both the perfluoroalkyl iodine (III) and iodine (V) fluorides decompose to give similar products. $C_4F_9IF_n$ (n = 2,4) decomposes to give C_4F_9I, C_4F_{10} and IF_5. Substantial amounts (5 - 20%) of R_FI and R_FF containing one to three carbon atoms can be isolated by gas chromatography and identified by time of flight mass spectrometry.

In this work, however, the preparation of the iodine (V) tetrafluorides, R_FIF_4, is not adequately characterised as they are not obtained pure, but contaminated with either solvent or the corresponding I(III) difluoride. As ClF_3 and CF_3I produced an unstable yellow solid which decomposes below 0^oC, the reaction was not fully investigated. The ^{19}F chemical shifts of the iodine (III) difluorides are at high field and can be used to distinguish them from the iodine (V) tetrafluorides but the spectroscopic properties of these compounds and in particular R_FIF_4, were not investigated fully. Hence a reinvestigation of the oxidation of perfluoroalkyl iodides seemed desirable, and as ClF_3 produced purer products it was extensively used in the following study.

The chemical properties, of chlorine trifluoride have been described by Ruff and Krug [77]. Since it is a vigorous fluorinating reagent, chlorine trifluoride reacts explosively with water and most organic compounds. Many elements ignite spontaneously in the trifluoride. Several metals and metaloxides also ignite and even the noble metals platinum, palladium and gold react at elevated temperatures [1]. It also reacts with the heaviest noble gases, xenon and radon, forming

xenon and radon fluorides. Nickel, Monel and Inconel are most resistant to attack by chlorine trifluoride at elevated temperatures, since they form adherent fluoride coatings, and copper is attacked only slightly below 300°C. Therefore, these metals along with mild steel, which is moderately corrosion resistant at room temperature, are often used by experimenters as container vessels for the liquid or gas. Although it is reported that Pyrex and quartz are slowly etched at room temperature, this may be due to hydrogen fluoride impurity, as it has also been stated that very pure ClF_3 has no effect.

Reactions of chlorine trifluoride with organic compounds have been reviewed by Musgrave [25]. Although organic compounds generally inflame or explode on contact with the trifluoride, the reactions may be moderated by diluting the interhalogen with an inert gas, by dissolving the organic compound in a relatively inert solvent, such as CCl_4 or a fluorocarbon, or by lowering the temperature. Substitution reactions, in which chlorine, bromine or iodine in organic halides are replaced by fluorine, are generally less exothermic and easier to control than reactions involving hydrocarbons. Cleavage reactions of C - C bonds can occur even with fluorocarbons, and violent explosions with relatively inert halocarbons, such as Kel-F oil, have been reported [1]. Chlorine trifluoride alone, and in the presence of catalysts, reacts with benzene to form mainly chlorobenzene and fluorobenzene. Some addition products, which by their analysis and reactions appeared to be chlorofluoro-cyclohexanes, -cyclohexenes, and -cyclohexadienes were formed as well, but generally in small quantities. Chlorine trifluoride can also act as a chlorinating and fluorinating agent towards sulphur. The gas diluted with nitrogen reacts with sulphur at room temperature in a flow system, producing SF_4, SCl_2 and S_2Cl_2. At high flow rates, SF_5Cl and SF_6 are also produced.

The aim of this study was to reinvestigate the preparation and properties of R_FIF_4 compounds, and to extend the range of those compounds already known, particularly to CF_3IF_4 and to aromatic derivatives. The scope of the reaction has been extended to study analogous bromine compounds and fluorocarbons containing two iodine atoms. The preparation of novel fluorocarbon compounds with both I(V) and S(VI) substituents has also been studied. To meet these objectives it was necessary to modify previous preparative methods employed by Rondestvedt. The structure of these compounds is of interest in that the sometimes very bulky perfluorocarbon group can occupy either an apical or equatorial site in the molecule, or a combination of isomers may be formed. In principle, the R_F group may be used as an n.m.r. probe to study the structural properties of these derivatives. By varying the R_F group, insight into reactivity of the parent iodide and subsequent reactivity of the corresponding tetrafluorides may be gained.

RESULTS AND DISCUSSION

The following reactions have been studied:

I. Preparation of Perfluoroalkyliodine (V) Tetrafluorides.

$CF_3I + ClF_3 \longrightarrow CF_3IF_4$

$CF_3I + ClF_3 \longrightarrow CF_3IF_2 + CF_3IF_4$

$C_2F_5I + ClF_3 \longrightarrow C_2F_5IF_4$

$(CF_3)_2CFI + ClF_3 \longrightarrow (CF_3)_2CFIF_4$

$n\text{-}C_4F_9I + ClF_3 \longrightarrow n\text{-}C_4F_9IF_4$

$ICF_2CF_2I + ClF_3 \longrightarrow F_2ICF_2CF_2IF_2 + F_4ICF_2CF_2IF_4$

II. Oxidation of Iodoperfluoroalkylsulphur (VI) Pentafluorides by ClF_3

$SF_5CF_2CF_2I + ClF_3 \longrightarrow SF_5CF_2CF_2IF_2 + SF_5CF_2CF_2IF_4$

$SF_5(CF_2CF_2)_2I + ClF_3 \longrightarrow SF_5(CF_2CF_2)_2IF_4$

III. Reactions of Perfluoroaromatic Halides with ClF_3

$C_6F_5I + ClF_3 \longrightarrow C_6F_5IF_4$

C_6F_5I + excess $ClF_3 \longrightarrow C_6F_5IF_4$ + ring chlorinated and fluorinated products.

$C_6F_5IF_4 + ClF_3 \longrightarrow$ Ring chlorinated and fluorinated products

$IC_6F_4I + ClF_3 \longrightarrow F_4IC_6F_4IF_4 + F_2IC_6F_4IF_2$?

$C_6F_5Br + ClF_3 \longrightarrow$ chlorinated and fluorinated ring products

IV. Reactions of R_FIF_4

$R_FIF_4 + CF_3CF{:}CF_2 \longrightarrow CF_3CFICF_3$ + decomposition products

$CF_3IF_4 + AsF_5 \longrightarrow CF_4 + X^+AsF_6^-$ $(X = IF_2^+?)$

CF_3IF_4 + pyridine $\longrightarrow$ molecular complex

CF_3IF_4 + acetonitrile $\longrightarrow$ molecular complex

CF_3IF_4 + dioxan $\longrightarrow$ molecular complex

$R_FIF_4 \xrightarrow{20^\circ C} R_FF + R_FI + IF_5 + I_2 + IF_3$?

$R_FIF_4 + H_2O \longrightarrow$ iodonium salt

V. Other Reactions

$C_3F_7Br + ClF_3 \longrightarrow$ no reaction

$n\text{-}C_4F_9I + CF_3OF \longrightarrow$ a mixture of fluorinated products + COF_2

I. Preparation of Perfluoroalkyliodine (V) Tetrafluorides

Oxidation of Perfluoroalkyl Iodides by Chlorine Trifluoride

Perfluoroalkyliodine (V) tetrafluorides, R_FIF_4 [R_F = CF_3, C_2F_5, $(CF_3)_2CF$, n-C_4F_9, $-CF_2CF_2-$] are formed from R_FI and ClF_3 in perfluorohexane solvent over the temperature range -78°C to -40°C in virtually quantitative fashion, according to equation 1.

$$3R_FI + 4ClF_3 \longrightarrow 3R_FIF_4 + 2Cl_2 \qquad 1$$

In order to obtain pure products, the addition of ClF_3 to the R_FI:C_6F_{14} mixture must be rigorously controlled. If the ratio of solvent to iodide is much below 3:1, exothermic and sometimes explosive reactions occur resulting in extensive C-I bond cleavage and the apparent formation of ClF and CF_4. Fast addition of ClF_3 also leads to exothermic reaction again with C-I bond cleavage. CF_4 and IF_5 are formed. Presumably, fast addition of ClF_3 leads to an accumulation of the liquid, which is not very soluble in C_6F_{14} at -78°C, in contact with the iodide causing the reaction to become uncontrollable. In most cases, when an exothermic reaction occurs, pure products are impossible to isolate. CF_3I is most sensitive to small changes in the amount of solvent and rate of addition of ClF_3 because it is the most volatile perfluoroalkyl iodide in the series, and initial reaction takes place in the gas phase and not in solution.

Under the reaction conditions employed, a sufficient excess of ClF_3 must be used to convert R_FI quantitatively to the tetrafluoride. Otherwise varying amounts of the perfluoroalkyliodine (III) difluoride are formed. Similarly, if the final reaction temperature is not about - 40°C or above, the difluoride is formed. On some occasions, mixtures containing varying amounts of CF_3IF_4 and CF_3IF_2 were formed. Oxidation of 1, 2-di-iodotetrafluoroethane also produced a mixture containing

both the 1, 2 bis iodine (III) difluoride tetrafluoroethane and the corresponding bis iodine (V) tetrafluoride. An efficient means of stirring the reaction mixture at low temperatures might allow complete conversion to the tetrafluoride. Attempts to prepare pure CF_3IF_2 proved unsuccessful, as the compound is unstable above 0^oC and only decomposition products are isolated. Preparation of the compounds R_FIF_2 [$R_F = C_2F_5$, $(CF_3)_2CF$, $n\text{-}C_4F_9$] was not investigated.

In view of the formation of CF_3IF_2, even when excess chlorine trifluoride is present, the oxidation of R_FI appears to be stepwise as follows:

$$R_FI \xrightarrow{ClF_3} R_FIF_2 \xrightarrow{ClF_3} R_FIF_4 \qquad 2.$$

with R_FIF_2 the initial product. Further reaction of R_FIF_2 with ClF_3 produces the tetrafluoride. Equation 2 suggests the formation of ClF as an initial product but this is only detected in certain occasions, when an exothermic reaction occurs. Formation of a complex between ClF and unreacted R_FI or R_FIF_2, or disproportionation in the reaction mixture to ClF_3 and Cl_2 may account for the gas not being detected. Conversion of a perfluoroalkyl iodide to its tetrafluoride in a one stage process requires at least, a termolecular reaction and these are uncommon. The above scheme suggests two bimolecular reactions are involved, which is more likely statistically. As the initial reaction between CF_3I and ClF_3 takes place in the vapour state, it is possible CF_3IF_2 is formed in a bimolecular gas phase reaction.

A complete discussion of the thermodynamics is not possible as the data are not available. Some insight into the thermodynamics of the system may be gained from the bond energies of the components of the system. The average bond energy of an I-F bond in IF_5 is 64·0 K cal mol^{-1} and the Cl-Cl bond energy is 58·2 K cal mol^{-1} in Cl_2[78.], whereas

the bond energy of a Cl-F bond in ClF_3 is 41·2 K cal mol $^{-1}$(1). On the basis of these data, the formation of R_FIF_4 and Cl_2 from R_FI and ClF_3 is favourable. The average C-F bond energy in CF_4 is 117 K cal mol $^{-1}$ and the C-I bond energy is approximately 51 K cal mol $^{-1}$ (C-I bond energy in CI_4 [167]). The formation of CF_4 from CF_3I is therefore favourable by some 66 K cal mol $^{-1}$, on bond energy data alone. Thus, rigorous control of reaction conditions is needed to prevent the occurrence of C-I bond cleavage.

Characterisation of Perfluoroalkyliodine (V) Tetrafluorides

These compounds are unstable with respect to decomposition and sensitive to moisture. They are best characterised by their spectra.

^{19}F n.m.r. spectra

Figure 1 shows a plot of the ^{19}F chemical shifts at room temperature of halogen fluorides against the oxidation state of the central halogen atom. The chemical shifts reported are, where possible, those of the equatorial fluorines and they are plotted as δ values relative to CCl_3F

Chemical Shift vs. Oxidation State in Halogen Fluorides.

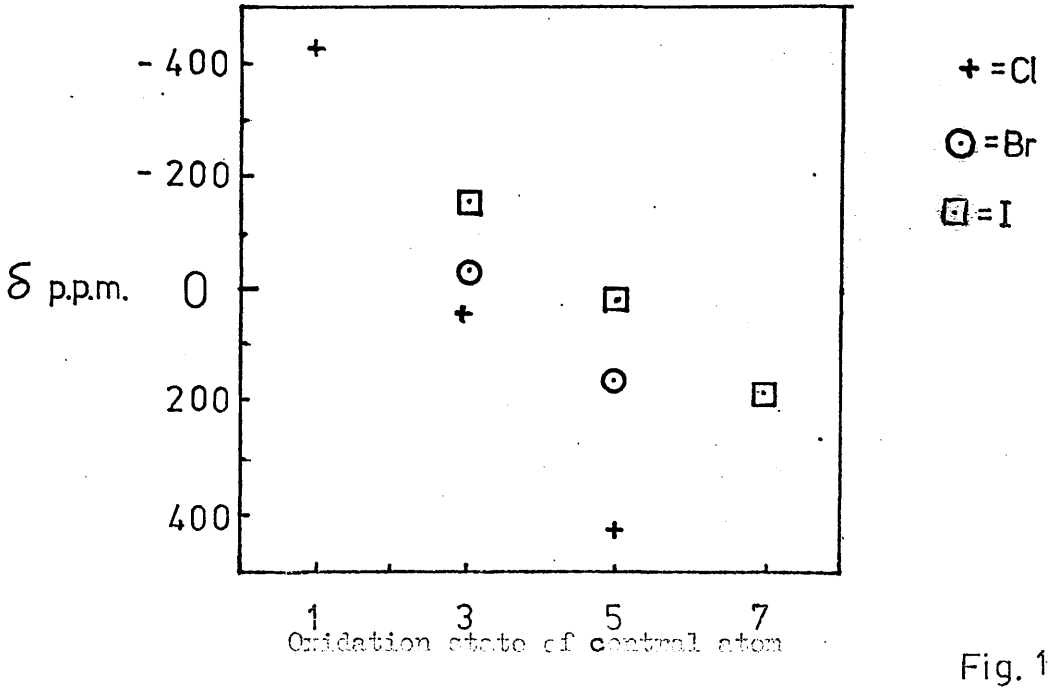


Fig. 1.

^{19}F N.M.R. SPECTRUM of CF_3IF_4 & CF_3IF_2

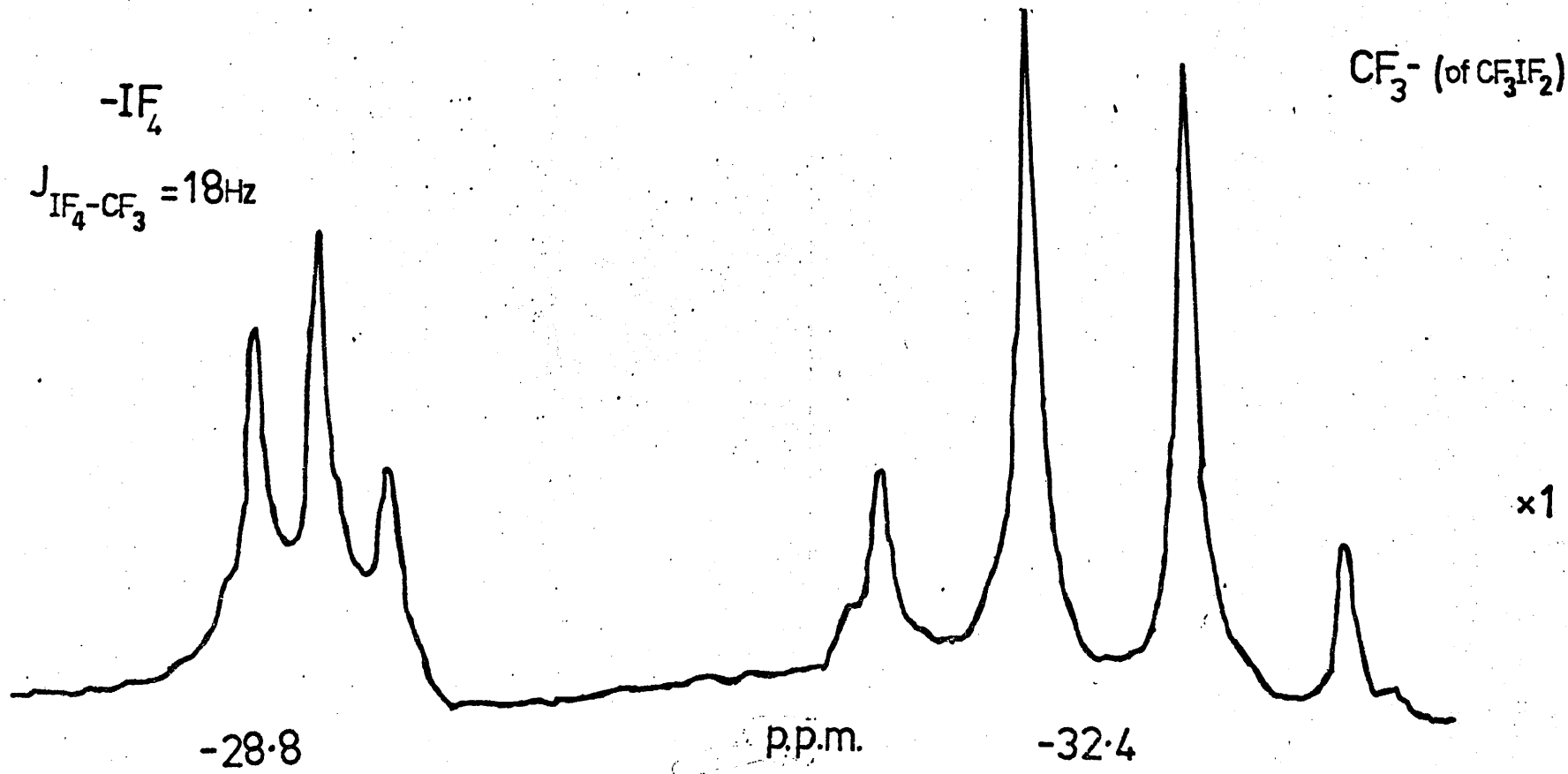


Fig. 2a.

^{19}F N.M.R. SPECTRUM of CF_3IF_4 & CF_3IF_2

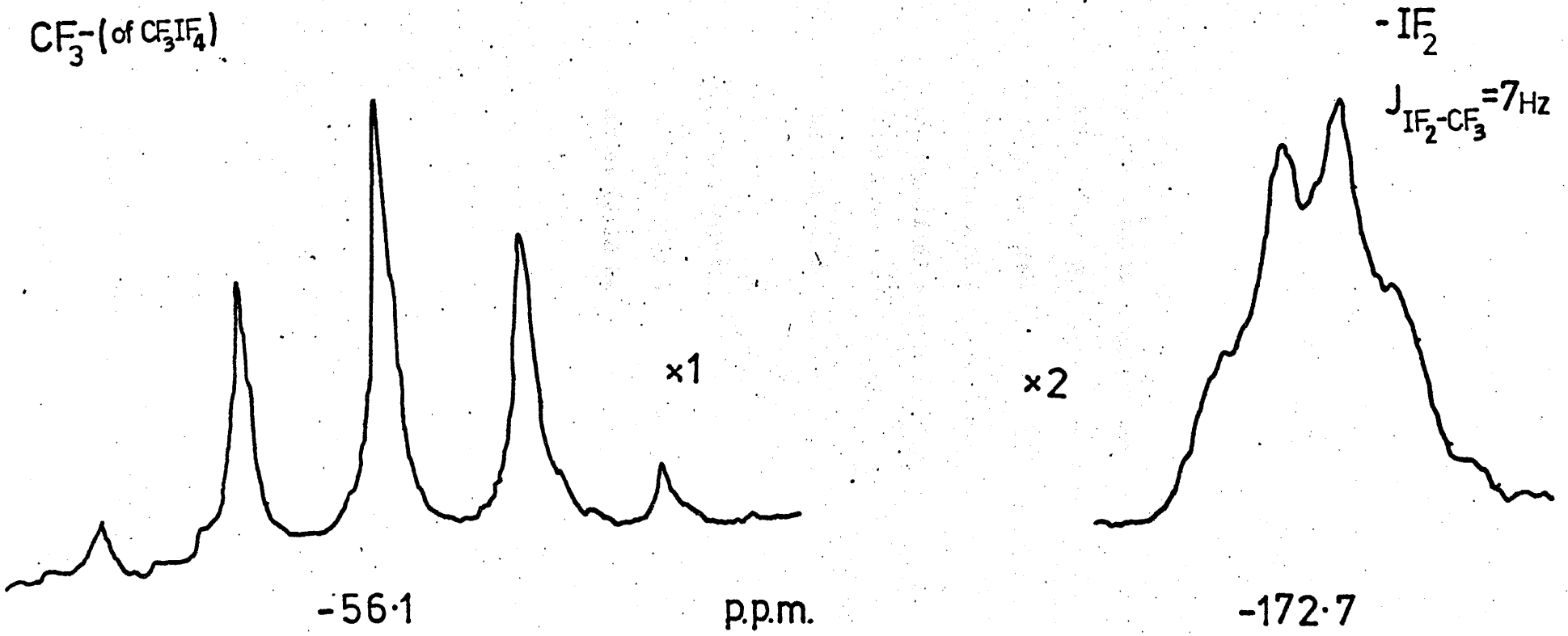


Fig.2b.

The chemical shift of fluorine - 19 in halogen fluorides varies as the central atom and also with the oxidation state of the central atom.

In some cases, the molecular structure of a binary fluoride can be confirmed from its n.m.r. spectrum. BrF_5, IF_5 and more recently ClF_5[79] have been shown to have a tetragonal pyramidal structure, their ^{19}F resonance spectra each consisting of two signals of intensity 4 : 1. Fine structure due to spin-spin coupling is observed and the quintet occurs at lower applied magnetic field. This lower shielding of the apex fluorine atom is attributed to the greater p covalent character of the axial bond compared to the equatorial bonds[80].

The chemical shifts of the identified R_FIF_n (n = 2,4) compounds are listed in Table 1. The chemical shifts of the parent iodides are added for comparison. Coupling constants and spin systems are tabulated in Table 2.

A pure sample of CF_3IF_4 in CCl_3F solution contains two signals. The assignments are made on the basis of a 1st order A_3X_4 spin system. The peak at δ-30·4 p.p.m. a quartet (J=18 Hz) is assigned to the IF_4 group and the quintet at -55·7 p.p.m. to the CF_3 group. The fluorine resonance of a mixture of CF_3IF_4 and CF_3IF_2 consists of four multiplets as shown in Fig. (2). The chemical shifts and coupling constants of the different species are easily extracted from the spectrum by comparison with a pure sample of CF_3IF_4. CF_3IF_2 is an A_3X_2 spin system. δ_A - 28·8, δ_X - 172·7 p.p.m., $J_{F_AF_X}$ = 8 Hz.

The ^{19}F n.m.r. spectrum of $C_2F_5IF_4$ in CCl_3F (Fig. 3) shows three multiplets. The resonance for the IF_4 group, δ - 30·2 p.p.m. is split into a triplet by the $-CF_2$ group δ-85·3 p.p.m., J=14 Hz, and each

^{19}F N.M.R. SPECTRUM of $C_2F_5IF_4$

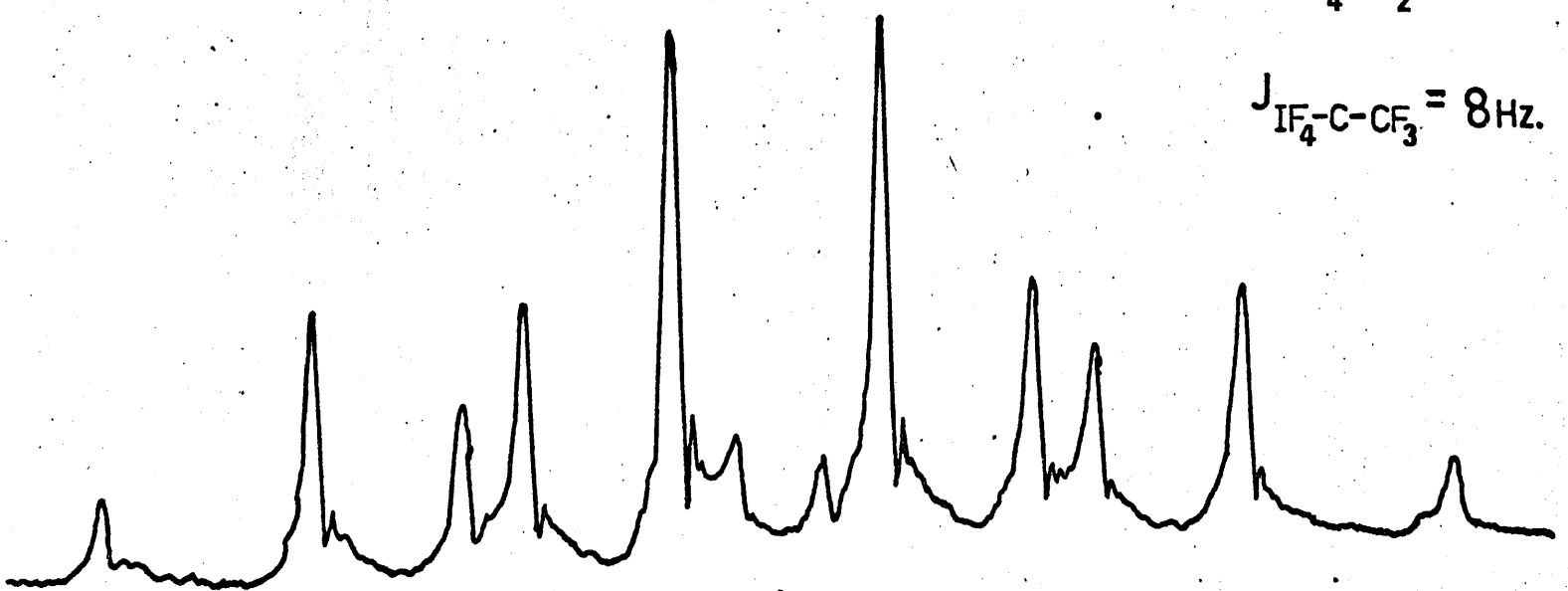


Fig.3a.

^{19}F N.M.R. SPECTRUM of $C_2F_5IF_4$

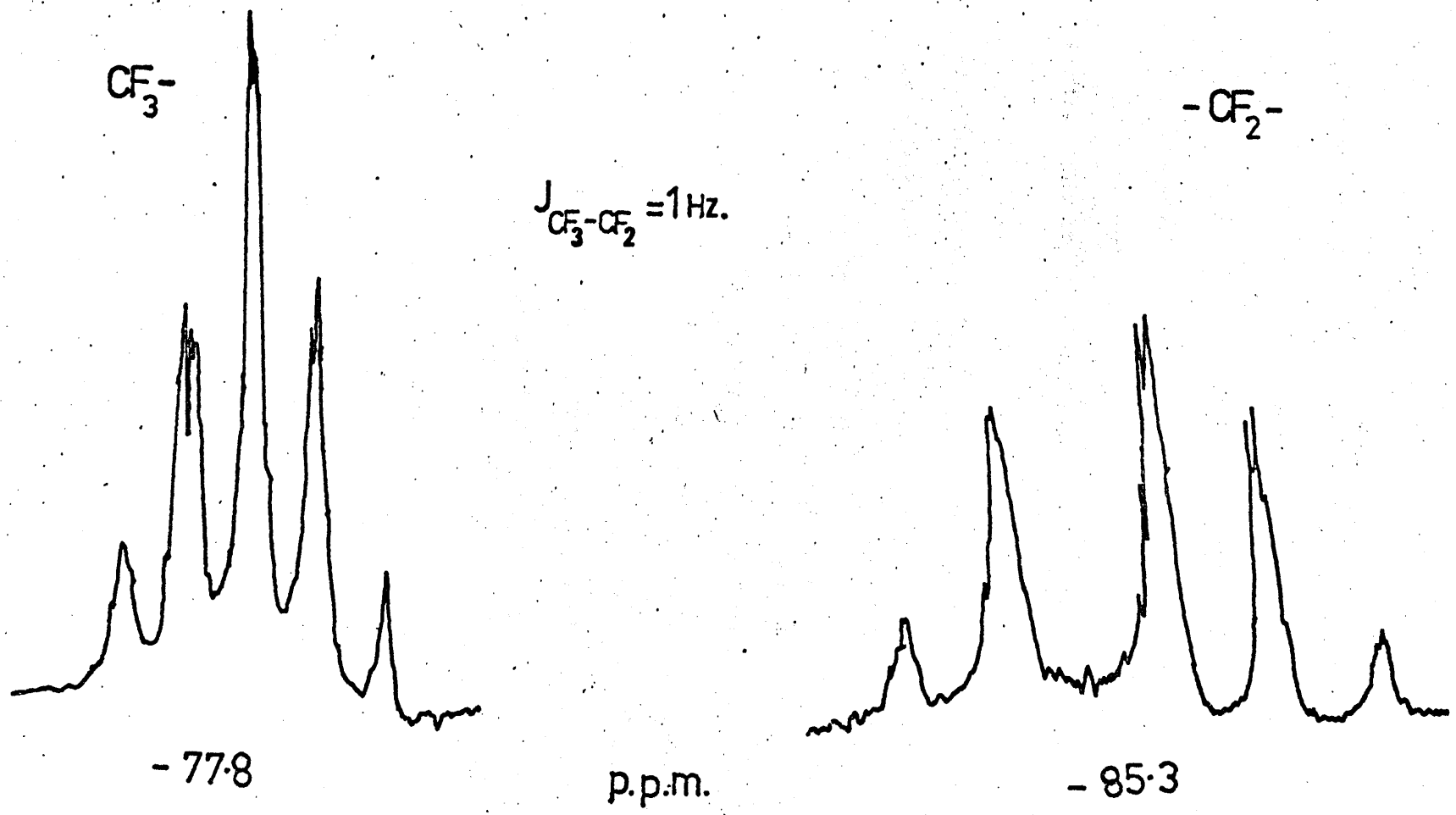


Fig.3b.

member of the triplet is split into a quartet due to coupling with the β-CF_3 group, δ-77·8 p.p.m. J=8Hz. Smaller splittings on the CF_2 and CF_3 resonance can be detected, J=1Hz. due to coupling between the α and β fluorines. The CF_2 group is a quintet of quartets and the CF_3 group is a quintet of triplets.

The spectrum of $(CF_3)_2$ $CFIF_4$ contains three multiplets. The IF_4 resonance, δ-17·3 p.p.m., appears to be an octet although only 6 peaks are clearly visible. This suggests the coupling to both the α and β fluorines is equal. The CF_3 group is a quintet of doublets due to coupling first with the four fluorines of the IF_4 group further split by coupling to the α fluorine. The high field unique α fluorine shows no fine structure but appears as a broad peak.

The fluorine resonance spectrum of $C_4F_9IF_4$ is more complex. It has been assigned the spin system $A_3M_2N_2P_2X_4$. A first order analysis, however, may not be appropriate in this case. The IF_4 group is easily identified as a low field quintet, δ_X - 29·2 p.p.m., J=16 Hz. The CF_3 group is assigned to the complicated triplet, δ - 82·2 p.p.m., J=11 Hz. The smaller spin coupling constants were not detectable on this resonance. The signal at δ - 81·1 p.p.m. is assigned to CF_2 α to the IF_4 group, principally because it is a quintet, J = 16 Hz and by analogy with the parent iodide. This signal overlaps with the CF_3 resonance to further complicate the spectrum. The two high field signals cannot be unambiguously assigned. The signal at δ - 124·0 p.p.m. is broad with no identifiable fine structure and the signal at δ - 129·3 p.p.m. is a complex triplet. The corresponding peaks in the parent iodide resonate at δ - 118·2 p.p.m. and δ - 129·9 p.p.m. but these signals are complicated as the spectrum is not 1st order. Therefore, they also cannot be unambiguously assigned. ^{19}F - ^{19}F double resonance

TABLE 1

^{19}F N.m.r. chemical shifts of perfluoroalkyliodine polyfluorides [a]

(δ values p.p.m.)

	CF_3I	CF_3IF_2	CF_3IF_4	C_2F_5I	$C_2F_5IF_4$	$(CF_3)_2CFI$	$(CF_3)_2CFIF_4$	n-C_4F_9I	n-$C_4F_9IF_4$	ICF_2CF_2I	$F_2ICF_2CF_2IF_2$	$F_4ICF_2CF_2IF_4$
IF_n		172·7	32·4		30·2		17·3		29·2		159.2	30·4
α	5	28·8	56·1	65·2	85·3	152·0	143·6	61·6	81·1	53·2	78·8	83·8
β				84·0	77·8	77·4	69·3	129·9	129·3			
γ								118·2	124·0			
δ								85·6	82·2			

[a] All chemical shifts upfield from CCl_3F int.

TABLE 2

$^{19}F - {}^{19}F$ Coupling constants of perfluoroalkyliodine polyfluorides

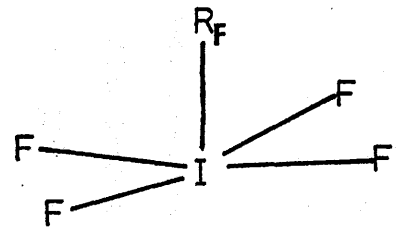
Compound	Spin System	Coupling Constants (Hz)		
		$^{3}J_{F-I-C-F}$	$^{4}J_{F-I-C-C-F}$	Others
CF_3IF_4	A_3X_4	18		
CF_3IF_2	A_3X_2	8		
$C_2F_5IF_4$	$A_3M_2X_4$	14	8	$^{3}J_{F_1F_2} = 1$
$(CF_3)_2CFIF_4$	A_6MX_4	11	11	$^{3}J_{F_1F_2} = 6$
$n\text{-}C_4F_9IF_4$	$A_3M_2N_2P_2X_4$ [a]	16	16	$^{4}J_{F_2F_4} = 11, {}^{3}J_{F_3F_4} < 1$
$F_4ICF_2CF_2IF_4$	A_4X_8 [a]	15	15	
$F_2ICF_2CF_2IF_2$	A_4X_4 [a]	9	9	

[a] may be second order spectra.

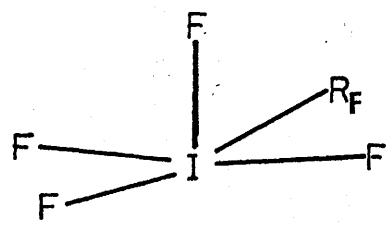
experiments on both the parent iodide and the tetrafluoride may aid these assignments. The appearance of the IF_4 group as a quintet suggests the iodine fluorines couple equally with two CF_2 groups. It seems reasonable to suppose that it is coupling to both the α and β CF_2 groups, although the coupling is not detected in either the signal at δ - 124·0 p.p.m. or the signal at δ - 129·3 p.p.m.

The n.m.r. spectrum of the product, in CH_3CN, obtained from the reaction between $C_2F_4I_2$ and ClF_3 indicate a mixture. IF_5 is a readily identifiable species, although the chemical shift of the doublet is approximately 5 p.p.m. upfield from pure IF_5. Signals at δ -30·4 and -83·8 p.p.m. are assigned to $F_4ICF_2CF_2IF_4$ by analogy with R_FIF_4 compounds and the F-F coupling constant, J_{FF} 15Hz and signals at δ-159·2 and -78·8 p.p.m. are assigned to $F_2ICF_2CF_2IF_2$ by analogy with R_FIF_2 compounds, J_{FF} being 9Hz. The spin systems have been analysed on a first order basis although they may in fact have a second order spin system of the type $A_2A_2'X_4X_4'$ and $A_2A_2'X_2X_2'$ respectively. Both the IF_4 (δ_x = -30·4 p.p.m.) and the IF_2 resonances (δ_x = -159·2 p.p.m.) are quintets implying that the iodine fluorines are coupled equally to the α and β CF_2 groups. The CF_2 resonance of $F_4ICF_2CF_2IF_4$ shows only seven of the nine predicted peaks and the CF_2 resonance of $F_2ICF_2CF_2IF_2$ indicates at least five peaks. The signal at δ - 139·0 p.p.m. is tentatively assigned to IF_3 although its chemical shift is very different from that for IF_3 produced in the decomposition of CF_3IF_4. The chemical shift of the IF_2 group is also to lower field than expected. These shifts are not readily explicable, but may be due to solvent effects. The production of IF_5 and possibly IF_3, in this preparation, is believed to be due to the presence of iodine in the starting material as no

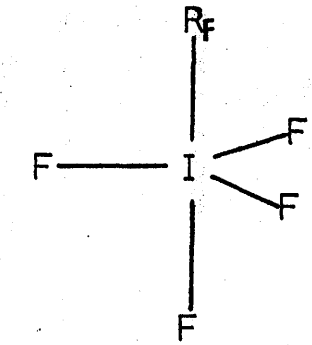
POSSIBLE STRUCTURES FOR R_FIF_4.



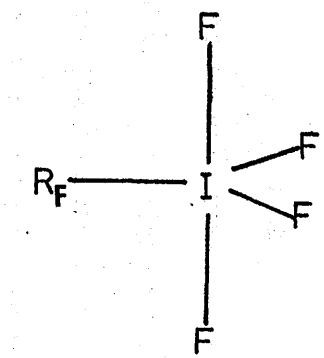
C_{4V} a



C_S b



C_{3V} c



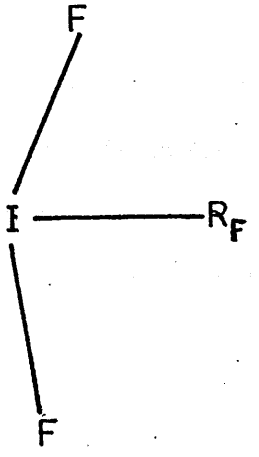
C_{2V} d

Fig. 4.

fluorocarbon fragments which could be produced from C-I bond cleavage were detected. No evidence of an unsymmetrically substituted derivative was obtained.

The IF_2 groups in R_FIF_2 occur at very high field, as expected from Figure 1, showing that the fluorines are strongly shielded. The IF_4 groups, in contrast, are relatively little shielded. No examples of coincidence between CF and IF resononances were observed. Therefore, the signals were usually easy to detect and assign. Only a single resonance attributable to $IF_n (n = 2,4)$ is observed suggesting that the fluorines are symmetrically arranged with respect to the R_F group. In the case of the tetrafluorides this implies the geometry is square pyramidal with the R_F group located in the apical position. However, rapid fluorine exchange, either inter - or intra-molecular, can also result in equivalence. For example, ClF_3 is known to have two equivalent and one unique fluorine atoms but is observed as a broad peak at 60°C [80]. The observation of F-C-I-F coupling at 20°C in R_FIF_4 is inconsistent with rapid inter-molecular fluorine exchange. Intra-molecular fluorine exchange preserves coupling and on the basis of the room temperature spectrum an equatorial R_F group or trigonal bipyramidal geometry (Fig. 4) cannot be excluded. Trigonal bipyramidal geometry requires that the lone pair becomes stereochemically inactive and for this reason it is not favoured. Also both the spectra of CF_3IF_4 and $C_2F_5IF_4$ are invariant down to -90°C when the solids precipitate from solution. It would be expected that at low temperatures different isomers could be separated out by slowing exchange. At 20°C, rigorously purified

ClF_3 has an AB_2 spectrum, and at -40°C, the spectrum contains a doublet and triplet consistent with an AX_2 system. It has also been reported [80] that the fine structure in the spectrum of IF_5 is lost only at 115° suggesting that fluorine exchange is not rapid at lower temperatures. Taking into account the invariance of the low temperature spectra of R_FIF_4 and the absence of rapid fluorine exchange in IF_5 at low temperatures, it is reasonable to propose that the structure of R_FIF_4 is square pyramidal with the R_F group occupying the unique axial position, structure a. By similar arguments, the structure of R_FIF_2 is C_{2v} (Fig. 5), or fast intramolecular fluorine exchange is occurring. It has been noted previously that the signals due to the IF_2 groups in both CF_3IF_2 and $F_2ICF_2CF_2IF_2$ are broad. This broadening may be due to coupling between fluorine and iodine. The rate of quadrupolar relaxation of the iodine must be intermediate between the rates in IF_5 and IF_7.



C_{2V}

Fig. 5

The chemical shifts of both the IF_2 and IF_4 groups resonate, in all cases, upfield from both the axial and equatorial fluorine

atoms in IF_5 and the signals assigned to IF_3. Similar shifts are observed in the sulphur-fluorine resonances of perfluoroalkyl sulphur polyfluorides. Examples are shown in Table 3. It should be noted that in the sulphur fluorine compounds these upfield shifts are most noticeable in those fluorines where the C - S - F bond angle approaches 90°

TABLE 3 [81]

Compound	$\delta_{F_{ax}}$	$\delta_{F_{eq}}$	δ_{CF_3}
CF_3SF_5	53·8	30·0	-62·4
CF_3SF_3	-50	-104	-72·7
CF_3SF	·→351		-58·
SF_6	57·0		
SF_4	71	118	

In this case the increased shielding may be due to an increase in the ionic character of the I - F bond.

The chemical shifts of the IF_4 group of R_FIF_4 do not vary considerably from δ - 30 p.p.m. when $R_F = CF_3$, C_2F_5, C_4F_9 or $F_4IC_2F_4$ but the chemical shift of IF_4 in $(CF_3)_2CFIF_4$ is -17·3 p.p.m. It appears that the chemical shift is insensitive to chain length, but depends to some extent on the degree of branching of the carbon bound to iodine. This anomalous behaviour of the perfluoroisopropyl group has also been observed in compounds of the type $(CF_3)_2CFX$ (X = Cl,Br, I). The fluorine bound to the same carbon atom as the other halogen shows a shift to higher field, the opposite behaviour to that found in a series of similarly substituted methanes [83].

The αCF_n groups (n = 2,3) of both the tetrafluorides and the difluorides are more shielded than in the corresponding iodides and the shielding is increased in going from I(III) to I(V). Similar behaviour is observed in SCF_3 of the sulphur derivatives listed in Table 3. As the oxidation state sulphur increases the CF_3 group shifts to higher field. In $C_2F_5IF_4$, the β fluorines are also shifted to higher field,but only slightly. This upfield shift can be ascribed to a decrease in the polarisability of $-IF_2$ and $-IF_4$ compared with -I in parent iodide. $(CF_3)_2 CFIF_4$ is also anomalous in this respect. Both α and β fluorines are shifted downfield.

The relatively large values of the β coupling constants may mean there is a contribution from "through space" coupling,as has been suggested for some coupling constants in highly fluorinated propane fragments and in some fluoroethylsulphur (Vl) pentafluorides [83]. Vicinal F-C-C-F constants are small and these were thought to reflect large spatial separation of the methyl and methylene fluorine nuclei in the pentafluoroethyl group (2·73 Å) [84]. However, if account is taken of the different relative signs of the various F - F coupling constants, the coupling behaviour cannot be co-related with internuclear distance in this simple manner. These anomalies may possibly be explained, then, as resulting from rotational averaging of trans and gauche coupling constants of opposite sign [85]. Ng and Sederholm [86] have suggested that F - F coupling operates by both "through bonds" and "through space"mechanisms . For geminal coupling constants both mechanisms are thought important; for vicinal coupling the "through bond" term is considered to be dominant and for coupling between nuclei separated by more than three bonds the spatial

mechanism is invoked.

Infrared and Raman Spectra.

The vibrationial spectroscopic data for the compounds, $R_F IF_4$, have been studied but the sampling methods have not been consistent. Comparison of frequencies over the range of sampling techniques cannot be accurately made but the outstanding feature of the condensed phase spectra is the appearance of a broad band or series of bands in the region 600 - 480 cm^{-1} which is charactistic of the IF_4 group. The remainder of the spectrum, in each case, is generally as expected for a fluorocarbon group bound to iodine.

The C - I stretching frequencies occur outside the range of the available i.r.sampling techniques but is observed in the Raman spectrum of CF_3IF_4.

The ^{19}F n.m.r. evidence suggests that the R_FIF_4 compounds possess nominal C_{4v} symmetry (Figure 4a). The spectra of $C_nF_{2n+1}IF_4$ are very complicated when $n > 1$ but a partial analysis of the gas phase i.r. and solid phase Raman spectra of CF_3IF_4 has been made. The CF_3 group can be assumed to be a single substituent X under conditions of a low or zero barrier to internal rotation of the CF_3 group against the IF_4 framework, which is a 12 fold barrier to rotation. The spectrum of CF_3SF_5 [87] obeys the selection rules derived for a molecule belonging to the C_{4v} point group. If the barrier to internal rotation is high, or if the R_F group is in fact situated in an equatorial position, the point group is C_s or lower. Thus, the vibrational spectrum of CF_3IF_4 may reasonably be expected to obey selection rules for a molecule of the type XIF_4 of C_{4v} symmetry

Group theory predicts that a molecule XIF_4 should have nine fundamental frequencies. For a tetragonal pyramidal molecule, all

TABLE 4

Infrared and Raman Spectra of CF_3IF_4 (cm^{-1})

I.R.(gas)	Raman (solid)	Assignment	CF_3I [88]		IF_5	
			I.R.	R.	I.R.[5]	R[6]
1260 vs		CF_3 antisym.stretch	1185	1168		
1237 m						
1187 m						
1068 vs	1054(3)	CF_3 sym.stretch	1073	1056		
1028 sh						
845 m						
760 sh						
756 s	754(5)	CF_3 sym.deformation	742	741		
750 sh						
736 sh						
646 m						
					710	705
599 vs		antisym.stretch			640	
	584(8)	Three IF_4 stretching				697[a]
	553(25)	modes and CF_3				600
	548(14)	deformation				578
	315(3)				374	375
	298(4)				315	316
	264(17)	C-I stretch	284	286		275
	220(2)					218[a]
	163(4)					191
	105(1)					

[a] not present in gas phase spectrum.

nine normal modes of vibration are Raman active but only six are infrared active. By reducing the symmetry to C_S all the fundamental modes become active in the Raman and the infrared. Added to these fundamental modes of the tetragonal pyramid are the modes due to the CF_3 group; the symmetric and antisymmetric C - F stretches, the symmetric and antisymmetric deformations and a CF_3 rocking mode similar to those found in CF_3SF_5. The spectra obtained were not inconsistent with C_{4v} symmetry but a complete analysis could not be performed as a suitable solvent could not be found, such that a polarised Raman could be run. A sample of CF_3IF_4 in CCl_3F decomposed in the laser beam and CH_3CN has been shown to complex with CF_3IF_4, and thus may distort the geometry. Also, the existing apparatus must be modified to perform a gas phase spectrum as the available vapour pressure is < 4mm Hg.

However, some band assignments can be made by comparison with the spectra of CF_3I [88], IF_5 [5,6] and CF_3SF_5 [87]. Table 4, lists the infrared and Raman spectra of CF_3IF_4 and the assignments which have been made. The spectra of IF_5 and some relevant bands in the spectra of CF_3I are included for reference. Other assignments cannot be made as definitively as those listed. There are four Raman bands in the region 300 - 100 cm^{-1} which may be due an out of plane bending and two deformation modes of the IF_4 group, and a CF_3 rocking mode by comparison with the spectrum of CF_3SF_5. There is a peak at 584 cm^{-1} in the Raman, and a broad envelope around 550 cm^{-1} which appears to contain at least two strong bands. A CF_3 deformation and three IF_4 stretching modes are expected in this region. In the Raman spectrum of liquid IF_5 an additional band is observed in

the IF stretching region at 697 cm^{-1} [6] (or 694 cm^{-1} [7]). It is attributed to association in the condensed states. It is not unreasonable, therefore, to expect a band in the Raman spectrum of CF_3IF_4 around 550 cm^{-1}, the IF stretching region in CF_3IF_4, and the broad envelope in this region may also contain a band attributable to this species. The absorption at 105 cm^{-1} (R) may correspond to the weak band at 218 cm^{-1} observed in the Raman spectrum of liquid IF_5, but which is also absent in the gas phase spectrum [6]. The bands at 1237, 1187, 1028, 845 and 646 cm^{-1} in the i.r. spectrum have not been assigned. Some of these bands, therefore, may be attributable to decomposition products of CF_3IF_4, as the compound decomposes slowly in contact with K Br, or possibly to combination bands.

The gas phase spectrum of a 1 : 1 mixture of CF_3IF_4 and CF_3IF_2 shows bands consistent with a CF_3 group and an IF_4 group. A strong band at 636 cm^{-1} is assigned to IF_5.

The gas and liquid infrared spectra of $C_2F_5IF_4$ are more difficult to interpret. The gas phase i.r. spectrum contains a sharp strong band at 600 cm^{-1} which can be assigned to the antisymmetric stretch of the IF_4 moiety. The bands at 1321, 1264, 1224, 1131, 919 and 749 cm^{-1} appear to be consistent with those expected by a C_2F_5 group bound to iodine, by comparison with the spectrum of C_2F_5I. Both the gas and liquid phase spectra contain a band around 850 cm^{-1}. This may be compared to the band at 845 cm^{-1} in the gas phase i.r. spectrum of CF_3IF_4 which is now tentatively assigned to a combination band. The liquid phase infrared spectrum of $C_2F_5IF_4$ shows a band at 641 cm^{-1} consistent with the antisymmetric stretch of IF_5. The IF_4 absorption is broad 600 - 520 cm^{-1}. This may indicate association in the

condensed phase.

Both the infrared spectra of $(CF_3)_2$ $CFIF_4$ and n-$C_4F_9IF_4$ are consistent with the presence of $(CF_3)_2$ CF- and n-C_4F_9- ligands respectively. The IF_4 absorption in both species ca. 600 cm^{-1} is broad. The spectrum of $(CF_3)_2$ $CFIF_4$ shows a significant extra band at 879 cm^{-1} and there is evidence of an extra band in the C - F absorption, although the region is broad. The spectrum of $C_4F_9IF_4$ has an extra band in the C - F stretching region at 1111 cm^{-1}. There also appears to be an extra band around 850 cm^{-1}. This band around 850 cm^{-1} seems to be present in all the spectra of the R_FIF_4 so far discussed. The mull i.r. spectra of the product from the solid obtained from the reaction of ICF_2CF_2I with ClF_3 shows several bands at 600 cm^{-1} and below, which can be attributed to the IF stretching frequencies. The remainder of the spectrum is comparable with an authentic spectrum of 1, 2,-di-iodotetrafluoroethane

Mass Spectra

The technique of mass spectrometry can be invaluable in dealing with complex mixtures of fluorine compounds just as it has been used to elucidate the composition and structure of complex mixtures of hydrocarbons [89]. The mass spectrometer aids the determination of molecular structure and the measurement of bond strengths. In determining molecular structure, a value for the molecular weight is obtained by finding the ion of highest mass in the spectrum of an unknown compound. Some compounds give only small molecular ion peaks or, as in the case of perfluoroparaffins for example, none at all, and then the highest peak in the spectrum is a fragment peak. The identification of molecular ion peaks may be facilitated by obtaining the spectrum at low ionizing voltage, a procedure which reduces

fragmentation and may even result, under favourable circumstances, in the formation of a single mass peak which is the molecular ion.

The greatest drawback to the unequivocal determination of molecular structure by mass spectrometry is the possibility of rearrangement during the ionization. McLafferty [90] has distinguished two types of rearrangement, random and specific. Random rearrangement occurs when several alternative reaction pathways have almost equal energy and entropy requirements, so that a number of rearranged ions are possible, usually of reduced abundance. Specific rearrangements are favoured when the molecule contains a functional group. Both types of rearrangement processes have been detected in fluorine compounds, although since fluorine is monoisotopic, it is not possible to study them by labelling.

One of the commonest rearrangement ions in the spectra of fluorocarbons is the presence of the CF_3^+ ion and its appearance in a spectrum is no indication that CF_3 is present in the unionized molecule. Price [89] considers that the CF_3^+ ion is planar and that ionization corresponds to the removal of the non-bonding p $-\pi$ electrons from the carbon atom. The ion is resonance stabilized, which lowers the energy involved in this process and results in the ionization potential being almost the same as for the methyl radical, despite the strong inductive effects of the fluorine atoms. The resulting ion has a closed shell configuration which makes it particularly stable and may account for its abundance in the mass spectra of fluorine compounds. The same considerations apply to the CF^+ ion which is also very abundant.

Certain modes of fragmentation are confirmed by the observation of metastable peaks in the mass spectrum. These are usually weak diffuse signals often appearing at non-integral masses. The process which causes the formation of these peaks is well understood. Ions of mass m, formed in the ionization chamber of the mass spectrometer are sufficiently stable to be withdrawn in large numbers from the ionization chamber, but their half-life is extremely short (10^{-5}-10^{-6}sec) and many of them dissociate to m_2^* during their passage to the collector. The kinetic energy of the m_2^* ion formed during flight (labelled m^*) is thus lower than that of m_2^* formed in the ion source. Consequently, the momentum of m^* is lower. It will be deflected to a greater extent in the magnetic field, and, therefore, be recorded lower down the mass range than m_2^* This breakdown in flight is known as a metastable transition and the recorded peak is a metastable peak. This peak is entirely characteristic of the metastable transition which gives rise to it and a mathematical formula can be derived which relates the ions m_1^*, m_2^* and m^* according to their masses. It approximates very closely to $m^* = (m_2)^2/m_1$.

The mass spectra (Appendix 1) of the parent perfluoroalkyl iodides and of iodine pentafluoride were recorded under similar conditions to the perfluoroalkyliodine (V) tetrafluorides. Unlike perfluoroparaffins, where the molecular ion is vanishingly small [89] the mass spectra of the perfluoroalkyl iodides under consideration show strong molecular ions and in the case of CF_3I, C_2F_5I and $(CF_3)_2$ CFI the molecular ion is the most abundant in the spectrum. The base peak in the spectrum of C_4F_9I is CF_3^+ and it is $C_2F_4^+$ in the spectrum of ICF_2CF_2I. An important fragmentation pathway in perfluoroalkyl iodides is scission

TABLE 5

Mass Spectra of R_FIF_4 compounds.

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		1. CF_3IF_4			
254	9	I_2^+	146	21	IF^+
215	< 1	CF_3IF^+	142	1	CH_3I^+
203	16	IF_4^+	139	1	CI^+
196	34	CF_3I^+	127	47	I^+
184	13	IF_3^+	69	100	CF_3^+
177	11	CF_2I^+	50	13	CF_2^+
165	70	IF_2^+	31	10	CF^+
158	< 1	CFI^+			
		2. $C_2F_5IF_4$			
265	1	$C_2F_5IF^+$	158	6	CFI^+
254	31	I_2^+	146	14	IF^+
246	43	$C_2F_5I^+$	142	2	CH_3I^+
227	14	I^+	139	2	CI^+
222	1	IF_5^+	127	46	I^+
208	1	$C_2F_3I^+$	119	67	$C_2F_5^+$
203	14	IF_4^+	100	28	$C_2F_4^+$
184	6	IF_3^+	69	100	CF_3^+
177	31	CF_2I^+	50	31	CF_2^+
165	19	IF_2^+	31	10	CF^+

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		3. $(CF_3)_2CFIF_4$			
334	<1	$(CF_3)_2CFIF_2^+$	165	1	IF_2^+
315	< 1	$(CF_3)_2CFIF^+$	158	1	CFI^+
296	41	$(CF_3)_2CFI^+$	150	22	$C_3F_6^+$
277	8	$C_3F_6I^+$	146	1	IF^+
254	24	I_2^+	131	14	$C_3F_5^+$
227	4	$C_2F_4I^+$	127	26	I^+
208	1	$C_2F_3I^+$	119	6	$C_2F_5^+$
203	< 1	IF_4^+	100	40	$C_2F_4^+$
196	< 1	CF_3I^+	93	4	$C_3F_3^+$
189	< 1	$C_2F_2I^+$	81	4	$C_2F_3^+$
184	< 1	IF_3^+	69	100	CF_3^+
181	8	IOF_2^+	50	6	CF_2^+
169	12	$C_3F_7^+$	31	17	CF^+
		4. n-$C_4F_9IF_4$			
346	19	$C_4F_9I^+$	196	1	CF_3I^+
327	1	$C_4F_8I^+$	184	1	IF_3^+
296	2	$C_3F_7I^+$	181	8	IOF_2^+
277	1	$C_3F_6I^+$	177	15	CF_2I^+
254	48	I_2^+	169	9	$C_3F_7^+$
246	1	$C_2F_5I^+$	165	1	IF_2^+
239	3	$C_3F_4I^+$	150	6	$C_3F_6^+$
232	1	$C_4F_3I^+$	146	1	IF^+
227	2	$C_2F_4I^+$	131	29	$C_3F_5^+$

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
222	1	IF_5^+	127	48	I^+
220	2	$C_3F_3I^+$	119	22	$C_2F_5^+$
219	35	$C_4F_9^+$	100	32	$C_2F_4^+$
213	1	$C_4F_2I^+$	93	5	$C_3F_3^+$
208	3	$C_2F_3I^+$	81	7	$C_2F_3^+$
203	2	IF_4^+	69	100	CF_3^+
201	1	$C_3F_2I^+$	50	8	CF_2^+
200	1	$C_4F_8^+$	31	22	CF^+

5. $F_4ICF_2CF_2IF_4$ / $F_2ICF_2CF_2IF_2$

411	< 0·1	$C_2F_7I_2^+$	170	1	C_2FI^+
392	0·1	$C_2F_6I_2^+$	146	27	IF^+
373	0·1	$C_2F_5I_2^+$	139	2	CI^+
354	15	$C_2F_4I_2^+$	127	100	I^+
265	1	$C_2F_6I^+$	119	47	$C_2F_5^+$
254	86	I_2^+	100	48	$C_2F_4^+$
246	20	$C_2F_5I^+$	82.5	3	$\frac{165}{2e}$
227	28	C_2F_4I	81	4	$C_2F_3^+$
222	8	IF_5^+	69	49	CF_3^+
208	46	$C_2F_3I^+$	63.5	1	$\frac{127}{2e}$
203	63	IF_4^+	62	2	$C_2F_2^+$
184	21	IF_3^+	50	30	CF_2^+
181	1	IOF_2^+	31	66	CF^+
177	22	CF_2I^+			

of the C - I bond,

$$R_F\overset{\frown}{-}\overset{\frown}{I}^+ \longrightarrow R_F^+ + I^\cdot$$

with the resulting formation of a perfluoralkyl radical ion. In fluorocarbon mass spectra the formation of R_F from R_FF is not an important process but the metastable transitions in several of the spectra recorded indicate that C - I bond cleavage occurs. The mass spectrum of IF_5, recorded via the gas inlet system of the mass spectrometer, shows an ion of large abundance due to I_2^+ which may be due to hydrolysis of IF_5. The base peak in the spectrum of IF_5 is IF_4^+, but only the radical ion IF_3^+ has a significant abundance of the other IF_n^+ ions (n = 1, 2). This may indicate the formation of an IF_3 species from IF_5 at 70eV ,

$$IF_5 \longrightarrow IF_3^+ + F^- + F^\cdot$$ [91] or possibly, IF_5

along with the iodine formed from hydrolysis in the source, yields trace quantities of IF_3 and this species ionizing gives rise to a relatively high abundance of IF_3^+.

Extensive fragmentation is observed in the mass spectra of these perfluoroalkyliodine tetrafluorides and tetrafluoride/difluoride mixtures. No molecular ions are observed in the spectra of any of the compounds even when the ionizing beam is reduced from 70eV to 20eV to 12eV (CF_3IF_4 and $C_2F_5IF_4$). At 12eV no ionization is observed. Table 5 lists the spectra at 70eV of the R_FIF_4 (R_F = CF_3, C_2F_5, $(CF_3)_2CF$, n-C_4F_9) and of the mixture obtained from the ICF_2CF_2I/ClF_3 reaction. Those spectra which were recorded at 20eV are listed in the experimental section and will not be further discussed. Although changes in intensities of several ions occur, no ions of mass $R_FIF_2^+$ are observed. The assignments on the mass

spectra are made assuming the bond energy of the C - F bond is greater than that of the I - F bond. Ions less than 0·5 relative abundance are not listed unless they are thought important in the characterisation of the compound.

Peaks of low intensity, which have been assigned to species R_FIF^+, are observed in all cases except where R_F is n-C_4F_9. For $(CF_3)_2CFIF_4$, a peak at $^m/_e$ = 334 is assigned to species $(CF_3)_2CFIF_2^+$. This may be indicative of the stability of the initial tetrafluoride. The spectrum of the $F_4ICF_2CF_2IF_4/F_2ICF_2CF_2IF_2$ mixture shows peaks of very low intensity, $^m/_e$ = 411, 392, 373 which are assigned to $C_2F_4I_2F_3^+$, $C_2F_4IF_2^+$ and $C_2F_4I_2F^+$. The location of the fluorines bonded to iodine cannot be established, but there appears to be no reason to suppose that they are not symmetrically arranged, where possible.

Although no metastables are observed, the principal fragmentation process appears to be loss of fluorine atoms from iodine. The peaks of highest abundance can all be attributed to the breakdown of the parent perfluoralkyl iodide and the metastables observed in these spectra correspond to those observed in the spectra of perfluoroalkyl iodides. Low intensity ions assigned to IF_4^+, IF_2^+ and IF^+ are detected in the spectra of all the tetrafluorides and the presence of these ions is considered characteristic of R_FIF_4. The above ions, especially IF_4^+, may indicate that a possible fragmentation process is cleavage of the C - I bond to form IF_4^+ and $R_F^\cdot$ as a neutral radical.

$$R_F\frown IF_4^+ \longrightarrow R_F^\cdot + IF_4^+$$

The presence of C_2F_5I in the spectrum of the mixture obtained from the ICF_2CF_2I/ClF_3 reaction indicates fluorine transfer from iodine to carbon. This is a favourable process energetically. Similar fluorine transfers

in R_FIF_4 would produce aliphatic fluorocarbons. These compounds, however, do not exhibit molecular ions but usually have CF_3^+ as a base peak [89]. It is of interest to note that, although in the spectra of R_FI [R_F = CF_3, C_2F_5, $(CF_3)_2CF$] the base peak is the molecular ion R_FI^+, in the corresponding tetrafluorides the base peak is $^m/_e$ 69, CF_3^+.

The positive ion mass spectra of these compounds are not definitive due to the absence of molecular ions and a complete rationalisation of the fragmentation process is impossible due to the complexity of the spectra. The high electronegativity of fluorine suggests that, even although the process is considered less favourable, negative ions, as well as positive ions, may form on electron bombardment of fluorine containing compounds. Negative ion mass spectra of fluorine compounds have been studied. The negative ion mass spectrum of SF_6 shows SF_6^- as an abundant ion whereas in positive ion spectrum SF_6^+ is not observed [92]. Therefore, by analogy, a negative ion mass spectrum of R_FIF_4 might provide molecular ion peaks.

II. Oxidation of Iodoperfluoroalkylsulphur (Vl) Pentafluorides

ClF_3 reacts smoothly with both $SF_5CF_2CF_2I$ and $SF_5(CF_2CF_2)_2I$ between -78°C and -40°C to produce bulky white solids. No evidence of extensive C - S or C - I bond cleavage is observed. The elemental analyses suggest that the products from both reactions are I(V) tetrafluorides but the ^{19}F n.m.r. spectrum of the product from $SF_5CF_2CF_2I$ and ClF_3 indicates a mixture of iodine (III) and iodine (V) fluorides.

^{19}F n.m.r. spectra

Table 6A lists the chemical shifts of the products in CH_3CN formed

TABLE 6

A. ^{19}F Chemical Shifts of $SF_5(CF_2)_mIF_n$ $\begin{Bmatrix} n = 2,4 \\ m = 2,4 \end{Bmatrix}$ (δ values p.p.m.)

	SF_{ax}	SF_{eq}	CF_2	CF_2	IF_n		
	+53·8	+46·8	-85·0	-60·1			
n = 2	56·6	+45.2	-95·8	-86·7	-175·5		
n = 4	56·6	+43·3	-95·8	-89·9	- 33·2		

B.

	SF_{ax}	SF_{eq}	CF_2	CF_2	CF_2	CF_2	IF_n
	+64·1	+45·3	-97·2	-125·3	-115·8	-60·3	
n = 4	+63·6	+45·3	-93·6	-121·4	-118·6	-85·1	-29·9

from $SF_5CF_2CF_2I$, together with the spectrum of $SF_5CF_2CF_2I$ itself. From the n.m.r. data the products were identified as $SF_5CF_2CF_2IF_4$ and $SF_5CF_2CF_2IF_2$ with the latter in slight excess, according to the relative intensities of the IF_4 and IF_2 resonances. Table 6B lists the chemical shifts of $SF_5(CF_2CF_2)_2$ IF_4 and the parent iodide. Assignments of IF_n (n = 2, 4) and CF_2 groups are made by analogy with R_FIF_2 and R_FIF_4. The chemical shifts of other CF_2 groups and SF_5 are made by analogy with R_FSF_5 [93]. The chemical shifts of the SF_5 groups are sufficiently downfield of other signals to avoid confusion. The SF_5 parameters, chemical shifts and coupling constants, are determined, where possible, from a second order analysis [94]. In the mixture $SF_5CF_2CF_2IF_4/SF_5CF_2CF_2IF_2$, the chemical shifts of the apical fluorines F_{ax} cannot be accurately determined as the predicted lines are not all observed. In the spectrum of $SF_5(CF_2CF_2)_2IF_4$, the signals at δ - 118·6 and -121·4 p.p.m. cannot be unambiguously assigned but the resonance at δ -118·6 p.p.m. shows evidence of fine structure (J = 16Hz) and is possibly coupled to the IF_4 group, which displays a similar coupling constant. This peak is therefore tentatively assigned to the CF_2 group β to IF_4. The signal at δ -121·4 p.p.m. is broad and no fine structure is detected.

The coupling constants detected on the IF_4 resonances are as expected, in $SF_5CF_2CF_2IF_4$ J = 16Hz, and in $SF_5(CF_2CF_2)_2IF_4$ J = 14 Hz. Both signals are quintets suggesting the IF_4 groups couple equally to the α and β CF_2 groups. The IF_2 resonance is broad, (width $\frac{1}{2}$-height 30 Hz.) and, although it shows evidence of fine structure, the coupling constants cannot be accurately determined. The CF_2 resonances are complicated due to coupling with both IF_4 and SF_5 groups. In the spectrum of

the $SF_5CF_2CF_2IF_4/SF_5CF_2CF_2IF_2$ mixture the CF_2 resonances are too complex to be analysed. $^{19}F - {}^{19}F$ decoupling experiment could simplify these spectra and aid assignment. In $SF_5(CF_2CF_2)_2IF_4$ the CF_2 group α to IF_4 is a quintet J=14 Hz and the CF_2 group α to SF_5 is a complex quintet J=22 Hz due to coupling with the equatorial fluorines and further coupling (J=6 Hz) to the apical fluorine. The coupling constant, $J_{F_{eq} - F_{ax}}$ in the I(V) compound is 140 Hz and $J_{F_{eq} - F_{ax}}$ in the I(III) compound is 95 Hz, in the $SF_5CF_2CF_2IF_4/SF_5CF_2CF_2IF_2$ mixture whereas in the parent iodide $J_{F_{eq} - F_{ax}}$ is 150 Hz. In $SF_5(CF_2CF_2)_2IF_4$ $J_{F_{eq} - F_{ax}}$ is 150 Hz, which is not significantly different from the parent iodide.

From Table 6 it can be seen that the chemical shift of the SF_5 group, particularly of the equatorial fluorines, is affected by the oxidation state of the iodine and the number of fluorines bound to iodine when only two CF_2 groups interpose between SF_5 and I. The equatorial fluorines move to higher field as the oxidation state of iodine increases from +1 in the parent iodide to +5 in iodine (V) tetrafluoride. When there are four CF_2 groups between the IF_4 and SF_5 groups no effect on the chemical shift of the SF_5 group is observed. This effect is probably transmitted through bonds and through space and it is likely that the SF_5 group in $SF_5(CF_2CF_2)_2IF_4$ is outside the influence of the IF_4 group.

Infrared and Raman Spectra

The infrared mull spectra of the $SF_5CF_2CF_2IF_4/SF_5CF_2CF_2IF_2$ mixture contains bands characteristic of the fluorocarbon and SF_5 moieties of the starting material. The bands are considerably broadened and some of the bands obvious in the parent iodide overlap to give broad bands in the product. The broad bands below 600 cm^{-1}

are characteristic of I - F stretching frequencies by comparison with previous spectra.

The infrared and Raman spectra of $SF_5(CF_2CF_2)_4IF_4$ are very complex and complete assignment is not possible but strong absorptions in the i.r. spectrum below 600 cm^{-1} are consistent with the presence of an IF_4 group. A broad envelope around 560 cm^{-1} in the Raman spectrum which contains at least two strong bands is assigned to IF_4 stretching modes by comparison with CF_3IF_4. The spectrum of CF_3SF_5[87] suggests that at least two modes due to the SF_5 group should also appear in this region. The strong sharp band at 686 cm^{-1} is assigned to an SF_4 symmetric stretch. The band at 717 cm^{-1} may be due to a skeletal mode of the carbon chain. The vibrational spectrum of the parent iodide has not been investigated and therefore it is difficult to obtain reliable data from the spectra of the product, as C - C, C - S, and C - F stretching modes appear over a wide range of frequencies [95]. The detailed spectra, although useful for characterisation of the compounds, were not used to obtain further structural information.

Mass Spectra

Assignments in the mass spectra of the compounds described above are not unambiguous as there are three types of fluorine in the compounds, SF, IF and CF. The relative band energies are S - F, 79 K cal mol^{-1} in SF_6[78]; I - F, 64 K cal mol^{-1} in IF_5; C - F, 117 K cal mol^{-1} in CF_4. Tentative assignments can be made using this data. However, the $^m/_e$ value of SF_5^+ and I^+ is 127 and peaks in which both can occur are not unambiguously assigned. The fragmentation of the SF_5 group by successive loss of F is apparent,

similar to the breakdown pattern in SF_6 [92]. The mass spectra of the mixture $SF_5CF_2CF_2IF_4/SF_5CF_2CF_2IF_2$ and of $SF_5(CF_2CF_2)_2IF_4$, have fragmentation ions characteristic of the parent iodide and IF_n^+ (n = 1,2,3,4). Similarly to the perfluoroalkyliodine (V) tetrafluorides previously discussed, both the spectra observed contain a peak of very small intensity attributable to $SF_5CF_2CF_2IF^+$ and $SF_5(CF_2CF_2)_2IF^+$, that is the parent iodide plus one fluorine suggesting that in these compounds also the major fragmentation pathway is loss of fluorine from iodine and subsequent breakdown of the iodide so formed. One interesting, but not readily understandable, feature of the spectra is that, although the base peak in both $SF_5(CF_2CF_2)_2I$ and the corresponding tetrafluoride is m/e 69, CF_3^+, the mass spectrum of the mixture $SF_5CF_2CF_2IF_4/IF_2$ contains SF_3^+ as a base peak whereas in the parent iodide $C_2F_5^+$ is the peak of highest abundance.

The spectroscopic data obtained on these pentafluorosulphur (VI) perfluoralkyliodine polyfluorides suggests the structure around the iodine nucleus is very similar to that of the perfluoroalkyl derivatives. In particular, the iodine (V) tetrafluorides have square pyramidal geometry with the alkyl side chain, bound to SF_5, in the axial position and four fluorines symmetrically positioned at the base. The iodine fluorines may, of course, be undergoing a rapid intramolecular rearrangement, but such a process is probably unlikely with such bulky substituents.

III. Reaction of Perfluoroaromatic Halides with ClF_3

(a) Reaction of C_6F_5I with ClF_3 - Characterisation of $C_6F_5IF_4$

ClF_3 reacts with C_6F_5I over the range -78°C to -15°C to produce $C_6F_5IF_4$ according to the equation:

$$3\ C_6F_5I + 4\ ClF_3 \longrightarrow 3\ C_6F_5IF_4 + 2Cl_2 \qquad 3.$$

$C_6F_5IF_4$ is isolated as a white solid, stable at 20°C, which is conveniently characterised by its elemental analysis and its ^{19}F n.m.r., mass and vibrational spectra.

TABLE 7

^{19}F chemical shifts (δ values) p.p.m.

	para F	meta F	ortho F	IF_4
C_6F_5I	-158·0	-165·4	-124·9	
$C_6F_5IF_4$	-143·3	-158·5	-128·9	-6·4

Table 7 lists the chemical shifts of $C_6F_5IF_4$ and C_6F_5I. Assignments of the aromatic fluorines were made by comparison with the parent iodide and in agreement with relative intensities; that is ortho: meta: para = 2: 2: 1. The ^{19}F n.m.r. spectrum of $C_6F_5IF_4$ contains a triplet (J = 26Hz) at δ -6·4 p.p.m. assigned to the IF_4 group and indicating coupling to the two ortho fluorines. The IF_4 group occurs ca. 24 p.p.m. to lower field in $C_6F_5IF_4$ than in perfluoroalkyl derivatives. This relative deshielding of the iodine fluorines is presumably due to steric, inductive and resonance effects of the

pentafluorobenzene ring. Inductively, the C_6F_5 group withdraws electrons from iodine along the C - I bond but it can also donate electron density into the unfilled d orbitals of the iodine depending on whether the IF_4 group is a π accepting or π donating ligand. If the overall effect is to increase the effective electronegativity of the iodine it can then withdraw more electron density from the fluorines, causing them to be deshielded. This argument, however, does not include the intramolecular electric field effects of the ortho fluorines, which are directed towards the iodine fluorines (Fig. 6).

The effect of a substituent, X, on the electronic distribution in C_6F_5X can be inferred from the chemical shifts of the nuclei attached to the ring [96]. It has been found that the ortho fluorine shift is influenced by a combination of inductive, steric and resonance effects, the meta shift mainly by inductive effects, the para fluorine mainly by resonance effects [96, 92], and that the para chemical shift is more sensitive to resonance effects than the ortho fluorine shifts. As the chemical shift of the para fluorine is often strongly influenced by the interaction of the π electrons of the aromatic ring with substituent X, it can be used as a probe in electronic studies on C_6F_5 X molecules. These chemical shifts are also subject to solvent effects.

Graham and his co-workers [98] have investigated a large number of pentafluorophenyl derivatives. They find a linear relationship between J_{op}, the coupling constant between the ortho and para fluorine atoms of the C_6F_5 group and δ_p, the chemical shift of the para fluorine. They suggest that the straight line relationship J_{op}-δ_p

distinguishes between π electron donation to the ring and π electron withdrawal from the ring by the substituent group. It is not possible to obtain the aromatic coupling constants of $C_6F_5IF_4$ as the signals due to the ortho, meta and para fluorines are complex and not well resolved. Therefore, J_{op} cannot be determined, but the downfield shift of the para fluorine in $C_6F_5IF_4$ relative to the parafluorine in C_6F_5I suggests that IF_4 is a better π electron acceptor than iodine. The interaction may be considered as a $p\pi \rightarrow d\pi$ interaction with d orbitals of iodine. It may be that there is a synergic effect with electron density being withdrawn from IF_4 along the C - I bond, as previously described, promoting back donation of π electrons into unfilled orbitals of iodine.

The meta fluorines, like the para, are also shifted downfield, 6·9 p.p.m., but the ortho fluorines move to higher field than in C_6F_5I. This upfield shift may be due to some sort of intramolecular electric field effect of the IF_4 group.

Infrared and Raman Spectra

The i.r. and Raman frequencies for $C_6F_5IF_4$ are listed in Table 8. $C_6F_5IF_4$ like CF_3IF_4 has been treated as an IF_4X species with C_{4v} symmetry, C_6F_5 being regarded as a point group. Excluding the ring modes, then, $C_6F_5IF_4$ should have nine fundamental frequencies, all nine Raman active but only six infrared active modes. However, regarding C_6F_5 as a point group may not be a good approximation as it is bulky and may invalidate some of the group theory predictions.

Many of the vibrational frequencies calculated for C_6F_5X (X =Cl, Br, I) are invariant as the mass of X changes [99]. The C - X stretching frequency, the C - X angle deformation mode and the C - F

TABLE 8

Infrared and Raman Spectra of $C_6F_5IF_4$

Infrared				Raman[a]	
cm^{-1}	Assignment	cm^{-1}	Assignment	cm^{-1}	Assignment
1638 m	Sym. ring stretch	626 m		626 (5)	
1520 sh	Antisym.ring stretch	588 s	IF_4 antisym.stretch	587 (18)	ring deformation mode
1503 s	Sym.C - F stretch	562 s	Ring deformation mode	576 (10)	IF_4 sym. and
1495 sh		545 sh		558 (13)	antisym stretches
1350 w		528 s		550 (13)	
1300 w	Sym.C-F stretch			538 (12)	
1268 w	ring stretching mode			482 (10)	ring stretch
1153 w	antisym.C-F stretch			443 (7)	ring angle deformation
1127 sh				405 (2)	
1099 s	sym.C-F stretch			385 (5)	
1059 w				310 (5)	
1004 s	Fermi			285 (5)	
987 s	Resonance			260 (4)	
807 sh	C-I stretch			223 (1)	
800 m				195 (11)	
722 m	Antisym.C-F deformation			170 (2)	
				90 (10)	
				80 (11)	

[a] Raman spectra obtained by J. Berry

angle deformation mode linked with a C - X angle deformation are the modes which display mass sensitive frequency changes. Therefore by comparing the spectra of $C_6F_5IF_4$ with those of C_6F_5I, several assignments can be made and these are also listed in Table 8.

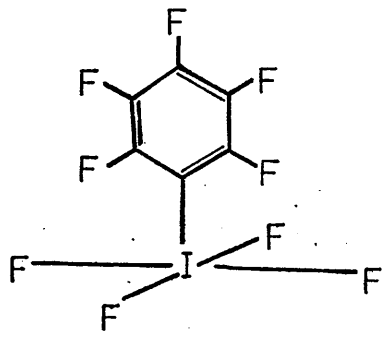
The bands in the i.r. spectrum of $C_6F_5IF_4$ attributable to ring modes are fairly consistent with those in C_6F_5I. The band at 800 cm^{-1} with a shoulder at 807 cm^{-1} is assigned to a C - I stretch. The broad absorption, containing at least four bands in the region 588 - 528 cm^{-1} is due to the IF_4 stretching frequencies and possibly a ring deformation mode which is predicted but not observed in the spectrum of C_6F_5I [99].

The Raman spectrum of $C_6F_5IF_4$, 600 - 50 cm^{-1} contains at least five strong bands in the region 581 - 538 cm^{-1}. Some of these are assigned to the IF_4 stretching frequencies, three expected in this region, and to a ring deformation mode. The band at 482 cm^{-1} is assigned to a symmetric ring stretching mode. The band at 443 cm^{-1} is assigned to a ring angle deformation mode by comparison with a similar band in C_6F_6 and C_6F_5Br. at 443 cm^{-1}. There are several bands in the region 385 - 120 cm^{-1} which may be due to an out of plane bending mode and two deformation modes of the IF_4 group, by comparison with the spectrum of IF_5, and several C - F and C - I angle deformations which are predicted to occur in this region.

Structure of $C_6F_5IF_4$

The ^{19}F n.m.r. and vibrational spectra are consistent with $C_6F_5IF_4$ having nominal C_{4v} symmetry with the aryl group in the axial position and four fluorines symmetrically positioned at the

base of a tetragonal pyramid. C_{4v} symmetry is preserved if the C_6F_5 group is freely rotating around the C-I bond as in R_FIF_4, previously discussed. The C_6F_5 group may, on the other hand, be rigidly positioned. If it is positioned such that the plane of the aromatic ring bisects the F-$\hat{I}$-F angle (Fig. 6), the four basal fluorines are still equivalent but the symmetry is reduced to nominal C_{2v}.



(Fig. 6)

Mass Spectrum of $C_6F_5IF_4$

The mass spectrum of $C_6F_5IF_4$, Table 9, contains a molecular ion $^m/_e$ 370 and peaks at $^m/_e$ 351, 332, 313 are readily assigned to $C_6F_5IF_3^+$, $C_6F_5IF_2^+$, $C_6F_5IF^+$. The base peak in the spectrum is attributed to $C_6F_5I^+$. Other ions of high abundance are consistent with the breakdown of $C_6F_5I^+$, as are the observed metastable transitions at 82·0 and 94·9.

$$C_6F_5^+ \longrightarrow C_5F_3^+ + CF_2^{\cdot} \qquad M^*_{calc.} = 81{\cdot}97$$

$$C_6F_5I \longrightarrow C_6F_5^+ + I^{\cdot} \qquad M^*_{calc.} = 95{\cdot}0$$

[100]

The mass spectra of aromatic fluorine compounds are well documented and have been reviewed [89]. Drakesmith and Jones [100] have reported metastable transitions in the mass spectra of fluoroaromatic compounds corresponding to loss of CF_3, CF_2 and CF fragments. The elimination of a CF_3 fragment is of interest in that it requires migration of two fluorine atoms to a carbon atom. The

TABLE 9

Mass Spectrum of $C_6F_5IF_4$

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
370	3	$C_6F_5IF_4^+$	167	58	$C_6F_5^+$
351	3	$C_6F_8I^+$	165	3	IF_2^+
332	1	$C_6F_7I^+$	148	18	$C_6F_4^+$
313	1	$C_6F_6I^+$	147	10	$C_6F_5I^{2+}$
394	100	$C_6F_5I^+$	146	1	IF^+
275	1	$C_6F_4I^+$	136	8	$C_5F_4^+$
263	1	$C_5F_4I^+$	127	28	I^+
254	6	I_2^+	117	56	$C_5F_3^+$
225	1	$C_5F_2I^+$	110	61	$C_6F_2^+$
203	1	IF_4^+	98	28	$C_5F_2^+$
186	7	$C_6F_6^+$	93	25	$C_3F_3^+$
184	1	IF_3^+	79	20	C_5F^+
			55	8	C_3F^+
			31	28	CF^+

formation of C_6F_6 in the spectrum of $C_6F_5IF_4$ suggests that there is migration of a fluorine atom from iodine to carbon. The absence of IF_5^+ implies the reverse process does not readily take place consistent with the relative bond strengths C-F>I-F.

Unlike the spectra of perfluoroalkyliodine (V) tetrafluorides the spectrum of $C_6F_5IF_4$ shows peaks which may contain I-F bonds other than R_FIF^+. This implies that species $C_6F_5IF_4^+$, $C_6F_5IF_3^+$ and $C_6F_5IF_2^+$ are more stable when the IF_n group is bonded to a pentafluorophenyl ligand. The precise position of the charge in a species $R_FIF_n^+$ has not been established but if it is located on the iodine, it may confer instability on the species with respect to other fragments. When R_F is C_6F_5, there is an opportunity for the charge to be resonance stabilised around the aromatic ring.

The Reaction of Pentafluorophenyl Iodide with excess Chlorine Trifluoride

Some preliminary experiments performed in collaboration with J. Berry show that when C_6F_5I is reacted with slightly more ClF_3 than required by equation (3), and the reaction mixture allowed to warm to room temperature, the product is not crystalline but is "mushy". The n.m.r. and mass spectra of this product contain peaks consistent with $C_6F_5IF_4$ but there are also fragments in the mass spectrum consistent with the replacement of a maximum of two ring fluorines by chlorine atoms. Peaks at $^m/_e$ = 402 and 386 have been assigned to species of the type $C_6F_3Cl_2IF_4^+$ and $C_6F_4ClIF_4^+$. These species may also result from products in which two Cl atoms have been added to the ring with subsequent loss of fluorine from carbon or iodine in the mass spectrometer but this is thought less likely. The appearance in some of the spectra of ions formulated as $C_5F_6Cl^+$ ($^m/_e$, 209), $C_5F_4Cl^+$ ($^m/_e$, 171) and $C_3F_4Cl^+$ ($^m/_e$, 147) strongly suggests that the

chlorine is bonded to carbon and not to iodine.

Reaction of C_6F_5I with a large excess of ClF_3 or the reaction of $C_6F_5IF_4$ with ClF_3 produces a viscous colourless liquid. The spectral data obtained on both products suggests that, although they are mixtures, the overall constitution of the products is very similar. The ^{19}F n.m.r. of the product from the reaction of $C_6F_5IF_4$ with ClF_3 contains a low intensity doublet at $\delta = +11{\cdot}5$ p.p.m. assigned to IF_5. The quintet is not observable. The presence of IF_5 indicates some cleavage of the C-I bond. A broad peak (width $\frac{1}{2}$-height = 140 Hz) at δ-5·5 p.p.m. is assigned to one or more IF_4 groups. No fine structure is observed on this signal. There are at least seven low intensity peaks from δ-80 to - 156 p.p.m. Peaks at δ-156, -147 and -137 p.p.m. may indicate an aromatic C_6F_5 group still present in the mixture whereas peaks between δ-147 and -80 p.p.m. are characteristic of olefinic fluorines and alicyclic CF_2 groups in a six membered ring.

The infrared spectrum of this liquid contains peaks consistent with $C_6F_5IF_4$ at 1634, 1500, ca 600 cm^{-1}. The presence of bands at 1780 and 1662 cm^{-1} is more characteristic of olefinic double bonded species. There are three strong intensity and many bands of smaller intensity in the region 1380 to 1150 cm^{-1}. These are consistent with C-F stretches of both alicyclic and olefinic fluorines in a six membered ring. Berry [101] reports that upon examination, the infrared spectrum of product (b), obtained from the action of 50% excess ClF_3 on C_6F_5I, shows marked similarities with the i.r. spectrum of dichlorooctafluorocyclohexane both in band position and band shape.

The mass spectrum of the product from the $C_6F_5IF_4/ClF_3$ reaction (Table 10) at a source pressure of 5×10^{-6} m.m. Hg indicates that a

TABLE 10

Mass Spectrum of Product from $C_6F_5IF_4$ + ClF_3 Reaction

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
462	< 1	$C_6F_{12}ClI^+$	171	8	C_5F_4Cl
443	<< 1	$C_6F_{11}ClI^+$	167	25	$C_6F_5^+$
424	< 1	$C_6F_{10}ClI^+$	165	27	$IF_2^+Cl^+$
421	< 1	$C_6F_9ClI^+$	164	<<1	$C_6F_3Cl^+$
408	< 1	$C_6F_9I^+$	162	14	$C_4F_6^+$
405	< 1	$C_6F_9ClI^+$	161	2	$C_6FCl_2^+$
402	< 1	$C_6F_7Cl_2I^+$	159	6	$C_4F_4Cl^+$
389	2	$C_6F_{10}I^+$	155	71	$C_5F_5^+$
386	< 1	$C_6F_8ClI^+$	148	7	$C_6F_4^+$
370	1	$C_6F_9I^+$	146	22	IF^+
351	3	$C_6F_8I^+$	145	<< 1	$C_6F_2Cl^+$
332	1	$C_6F_7I^+$	143	14	$C_4F_5^+$
313	1	$C_6F_6I^+$	142	2	$C_6Cl_2^+$
294	3	$C_6F_5I^+$	136	16	$C_5F_4^+$
277	1	$C_3F_6I^+$	131	15	$C_3F_5^+$
262	< 1	$C_6F_{10}^+$	129	2	$C_6F_3^+$
256	< 1	$C_6F_6Cl_2^+$	127	59	I^+
243	5	$C_6F_9^+$	124	21	$C_4F_4^+$

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
227	1	$C_2F_4I^+$	117	100	$C_5F_3^+$
224	1	$C_6F_8^+$	112	5	$C_3F_4^+$
222	< 1	IF_5^+	110	3	$C_6F_2^+$
221	2	$C_6F_6Cl^+$	105	14	$C_4F_3^+$
209	7	$C_5F_6Cl^+$	100	3	$C_2F_4^+$
205	27	$C_6F_7^+$	98	26	$C_5F_2^+$
203	19	IF_4^+	93	86	$C_3F_3^+$
202	1	$C_6F_5Cl^+$	86	17	$C_4F_2^+$
193	5	$C_5F_7^+$	79	20	C_5F^+
190	2	$C_5F_5Cl^+$	74	25	$C_3F_2^+$
186	36	$C_6F_6^+$	69	51	CF_3^+
184	18	IF_3^+	62	2	$C_2F_2^+$
180	1	$C_6F_2Cl_2^+$	55	10	C_3F^+
178	4	$C_4F_5Cl^+$	50	5	CF_2^+
174	23	$C_5F_6^+$	31	53	CF^+

METASTABLE TRANSITIONS

m_1	Transition	m_2	calc. m^*	found
243	$C_6F_9^+ \rightarrow C_5F_7^+ + CF_2^\cdot$	193	153·0	153·0
224	$C_6F_8^+ \rightarrow C_3F_6^+ + CF_2^\cdot$	174	135·7	135·9
224	$C_6F_8^+ \rightarrow C_5F_5^+ + CF_3^\cdot$	155	107·2	107·3
205	$C_6F_7^+ \rightarrow C_5F_5^+ + CF_2^\cdot$	155	117·1	117·0

m_1	Transition	m_2	calc. m^*	found
136	$C_6F_4^+ \rightarrow C_5F_3^+ + F^\cdot$	117	100·7	100·8
186	$C_6F_6^+ \rightarrow C_5F_4^+ + CF_2^\cdot$	136	99·4	99·4
294	$C_6F_5I^+ \rightarrow C_6F_5^+ + I^\cdot$	167	95·0	94·8
167	$C_6F_5^+ \rightarrow C_5F_3^+ + CF_2^\cdot$	117	81·9	82.0
186	$C_6F_6^+ \rightarrow C_5F_3^+ + CF_3^\cdot$	117	73·8	73·8
148	$C_6F_4^+ \rightarrow C_5F_2^+ + CF_2^\cdot$	98	64·9	65·0
254	$I_2^+ \rightarrow I^+ + I^\cdot$	127	63·5	63·7

mixture is present. The chlorinated species in this spectrum suggest that the ring products contain a maximum of two chlorine atoms. Some of the fragments containing ^{35}Cl atoms are formulated as $C_6F_4ClIF_4^+$ $^m/_e$ 405, $C_6F_3Cl_2IF_4^+$, $^m/_e$ 402 and $C_6F_4ClIF_4^+$, $^m/_e$ 386. There are also peaks of smaller intensity at $^m/_e$ 421, $C_6F_5Cl_2IF_4$; $^m/_e$ 424, $C_6F_6ClIF_4^+$; and $^m/_e$ 462, $C_6F_{10}ClIF_4$. Reasonably strong signals at $^m/_e$ 186, $C_6F_6^+$; $^m/_e$ 205, $C_6F_7^+$; $^m/_e$ 224, $C_6F_8^+$; and $^m/_e$ 243, $C_6F_9^+$, are consistent with the benzene ring being fluorinated. Metastable transitions listed in Table 10 confirm the presence of these species and indicate that loss of CF_3, CF_2, CF and F is important in the further fragmentation of these ions in common with cyclic fluorocarbons. The presence of species formulated as $C_6F_6IF_4^+$, $^m/_e$ 389 and $C_6F_7IF_4^+$, $^m/_e$ 408 imply that ring fluorination can also occur without cleavage of the C-I bonds. No metastable transitions are observed for the breakdown of $C_6F_nIF_4$ ($n \geq 6$) so that no definite conclusions can be drawn about the structure or fragmentation pathway of these ions.

The Reaction between 1,4-Diiodotetrafluorobenzene and Chlorine Trifluoride

The reaction between ClF_3 and $C_6F_4I_2$ produces a bulky white solid insoluble in CH_3CN, IF_5, C_6F_6 and CCl_3F. As no suitable solvent was found, the ^{19}F n.m.r. spectrum of the product was not obtained.

Comparison of the i.r. spectrum with that of the parent iodide indicates several strong bands below 580 cm^{-1}. In particular a strong fairly broad band is observed at 476 cm^{-1}. This band along with some of the others may be due to IF_4 stretching modes. In the product two bands appear at 590 cm^{-1} and 570 cm^{-1} compared to one band at 580 cm^{-1} in the starting material. The other significant difference is the appearance of a strong band at 1236 cm^{-1}. This band is thought to be a combination band (758 + 476 cm^{-1}) by

TABLE 11

Mass Spectrum of Product from $C_6F_4I_2$ and ClF_3

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
554	0.6	$C_6F_4(IF_4)_2^+$	174	1	$C_5F_6^+$
535	1	$C_6F_{11}I_2^+$	170	2	C_2FI
516	1	$C_6F_{10}I_2^+$	167	43	$C_6F_5^+$
497	4	$C_6F_9I_2^+$	165	9	IF_2^+
478	10	$C_6F_8I_2^+$	162	1	$C_4F_6^+$
459	4	$C_6F_7I_2^+$	155	1	$C_5F_5^+$
440	4	$C_6F_6I_2^+$	148	100	$C_6F_4^+$
421	3	$C_6F_5I_2^+$	146	11	IF^+
402	53	$C_6F_4I_2^+$	136	3	$C_5F_4^+$
389	3	$C_6F_6IF_4^+$	129	14	$C_6F_3^+$
370	0.7	$C_6F_9I^+$	127	49	I^+
351	5	$C_6F_8I^+$	117	86	$C_5F_3^+$
332	2	$C_6F_7I^+$	110	10	$C_6F_2^+$
313	1	$C_6F_6I^+$	98	67	$C_5F_2^+$
294	47	$C_6F_5I^+$	93	17	$C_3F_3^+$
275	22	$C_6F_4I^+$	91	2	C_6F^+
256	2	$C_6F_3I^+$	86	6	$C_4F_2^+$
254	18	I_2^+	79	45	C_5F^+
224	5	$C_6F_8^+$	74	12	$C_3F_2^+$
205	14	$C_6F_7^+$	69	3	CF_3^+
203	5	IF_4^+	67	2	C_4F^+
202	38	$C_3F_2I^+$	60	2	C_5
186	45	$C_6F_6^+$	55	7	C_3F^+
184	3	IF_3^+	50	1	CF_2
181	1	IOF_2^+	36	1	C_3
			31	26	CF

METASTABLE TRANSITIONS

m_1	Transition	m_2	m^* Calc.	m^* found
554	$C_6F_4(IF_4)_2^+ \longrightarrow C_6F_5IF_4^+ + IF_3^{\cdot}$	370	247	247
167	$C_6F_5^+ \longrightarrow C_5F_4^+ + CF^{\cdot}$	136	110.4	110.5
294	$C_6F_5I^+ \longrightarrow C_6F_5^+ + I^{\cdot}$	167	95.0	94.9
167	$C_6F_5^+ \longrightarrow C_5F_3^+ + CF_2^{\cdot}$	98	81.9	82.0
186	$C_6F_6^+ \longrightarrow C_5F_3^+ + CF_3^{\cdot}$	98	73 6	73.8

comparison with the bands at ca 850 cm^{-1} in the spectra of the perfluoroalkyliodine (V) tetrafluoride. The band at 758 cm^{-1} can be assigned to a C-I stretch. Due to the simplicity of the spectrum it seems no fluorination or chlorination of the benzene ring has occurred.

The mass spectrum Table 11 of the solid indicates that both iodines are oxidatively fluorinated to the tetrafluoride, although the corresponding I (III)compound may also be present. The assignment of peaks at $^{m}/e$ 554, 535, ...,421 is made on the basis that for the reaction between C_6F_5I and ClF_3 fluorination of the iodine occurs before addition of fluorine to the aromatic ring. The fluorocarbon fragments which contain more than four fluorines per aromatic ring can again be explained by invoking transfer of fluorine from iodine to carbon. For example, the diffuse, low intensity metastable at ca. $^{m}/e$ 247 corresponds to the transition

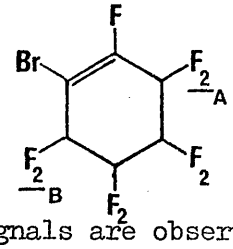
$$C_6F_4(IF_4)_2^+ \longrightarrow C_6F_5IF_4^+ + IF_3$$

Although no metastable transitions are observed, other fluorine transfer processes can produce species of the type $C_6F_6IF_4^+$, $^{m}/e$ 389; $C_6F_8^+$, $^{m}/e$ 224; $C_6F_7^+$, $^{m}/e$ 205; $C_6F_5I^+$, $^{m}/e$ 47; etc. Other peaks in the spectrum are consistent with the breakdown of the aforementioned species and of $C_6F_4I_2$ itself. No evidence of chlorination of the ring is observed in the mass spectrum.

The Reaction of Bromopentafluorobenzene with Chlorine Trifluoride

ClF_3 reacts with C_6F_5Br to produce a mixture of products. Signals in the ^{19}F n.m.r. of the liquid product at δ-160·1, -154·0, -132·3 p.p.m. indicate that the major constituent of the liquid is unreacted C_6F_5Br. The appearance of many other peaks in the spectrum indicate that there are several minor reaction products all of which contain different types of fluorine, alicyclic, olefinic and conjugated

olefinic fluorines. In particular, resonances at δ -108·3 and -119·4 p.p.m. compare with those reported for the molecule C_6F_9Br.



δ_A = -119·4 p.p.m.

δ_B = -108·3 p.p.m. 113.

No signals are observed in the regions expected for Br(III) and Br(V) fluorides.

The infrared spectrum of the mixture shows C_6F_5Br to be a major constituent. There are several strong bands in the region 1365 to 1100 cm^{-1} which are very similar to those in the highly fluorinated products obtained in the reaction between $C_6F_5IF_4$ and ClF_3. The spectrum contains many bands in the region 1100-600 cm^{-1}, four of which are assigned to C_6F_5Br modes, 1089, 1004, 976 and 834 cm^{-1}. Some of the other bands may be due to C-Cl stretches. There are no bands in the spectrum which can be unambiguously correlated with the modes observed in BrF_3, which has strong absorptions at 1337 and 613 cm^{-1}, or BrF_5, 1362, 1258, 1195, 820 and 644 cm^{-1} (1)

The mass spectrum of the product shows ions consistent with the fragmentation of C_6F_5Br. The peak at $^m/_e$ 338, assigned to $C_6F_8{}^{79}Br{}^{35}Cl^+$ implies that addition of both F and Cl to the ring occurs. The mass spectrum of BrF_5 contains the expected fragments, BrF^+, BrF_2^+, BrF_3 and BrF_4^+ (1). The absence of peaks which exhibit the ^{79}Br, ^{81}Br isotope pattern at $^m/_e$ 155, 157, BrF_4^+ and $^m/_e$ 136, 138, BrF_3^+ suggests that no oxidative fluorination of Br has taken place, and the peaks at $^m/_e$ 155 and $^m/_e$ 136 can readily be assigned to fluorocarbon fragments $C_5F_5^+$ and $C_5F_4^+$, respectively. Peaks at $^m/_e$ 322, 303, 284, 265 are therefore assigned to $C_6F_9{}^{79}Br^+$, $C_6F_8Br^+$, $C_6F_7Br^+$ and $C_6F_6Br^+$ and not to the isomeric structures $C_6F_8BrF_4^+$ etc. The

TABLE 12

Mass Spectrum of Product from C_6F_5Br/ClF_3 reaction

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
338	1	$C_6F_8ClBr^+$	147	1	$C_3F_4Cl^+$
322	1	$C_6F_9Br^+$	136	8	$C_5F_4^+$
303	1	$C_6F_8Br^+$	131	9	$C_3F_5^+$
284	18	$C_6F_7Br^+$	129	1	$C_6F_3^+$
265	5	$C_6F_6Br^+$	124	4	$C_4F_4^+$
259	2	$C_6F_8Cl^+$	117	32	$C_5F_3^+$
246	3	$C_6F_3Br^+$	110	1	$C_6F_2^+$
243	2	$C_6F_9^+$	98	8	$C_5F_2^+$
224	3	$C_6F_8^+$	93	21	$C_3F_3^+$
209	1	$C_5F_6Cl^+$	85	7	CF_2Cl^+
205	66	$C_6F_7^+$	81	3	$Br^+, C_2F_3^+$
186	42	$C_6F_6^+$	79	7	Br^+, C_3F^+
171	1	$C_5F_4Cl^+$	74	8	$C_3F_2^+$
167	10	$C_6F_5^+$	69	100	CF_3^+
155	46	$C_5F_5^+$	55	4	C_3F^+
148	2	$C_6F_4^+$	50	3	CF_2^+
			31	27	CF^+

Metastable Transitions

m_1	Transition	m_2	m^* calc	m^* found
205	$C_6F_7^+ \rightarrow C_5F_6^+ + CF^{\cdot}$	174	147·6	147·5
340	$C_6F_8{}^{37}Cl^{79}Br^+ \rightarrow C_5F_6{}^{37}Cl^+ + CF_2Br^{\cdot}$	211	130·9	130·7
338	$C_6F_8{}^{35}Cl^{79}Br^+ \rightarrow C_5F_6{}^{35}Cl^+ + CF_2{}^{79}Br^{\cdot}$	209	129·2	129·6
205	$C_6F_7^+ \rightarrow C_5F_5^+ + CF_2^{\cdot}$	155	117·1	117·3
136	$C_6F_4^+ \rightarrow C_5F_3^+ + F^{\cdot}$	117	100·7	100·8
186	$C_6F_6^+ \rightarrow C_5F_3^+ + CF_2^{\cdot}$	117	73·6	73·8

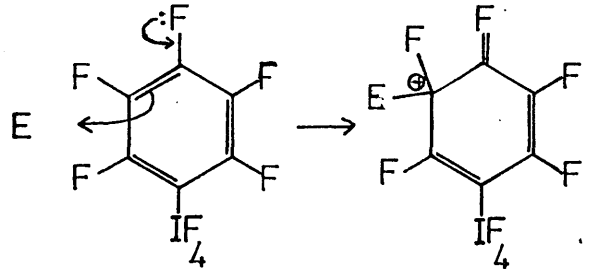
presence of $C_6F_9Br^+$ is consistent with the presence of the bromofluorocyclohexene indicated by the ^{19}F n.m.r. spectrum.

A mixture of BrF_3 and Br_2 reacts with C_6F_6 to give octafluorocyclohexa -1, 4, - diene and 4 - bromononafluoro cyclohexene, the latter being the major product [102]. From bromopentafluorobenzene is obtained 1-bromoheptafluorocyclohexa - 1, 4 - diene and a mixture of dibromooctafluorocyclohexene isomers. An excess of the BrF_3/Br_2 mixture also produces a mixture of tribromononafluorocyclohexane isomers. The reaction of pentafluoro - benzene itself gives, in addition to bromopentafluorobenzene, the diene, olefin and tribromocyclohexane identical with that obtained by the bromo-fluorination of bromopentafluorobenzene. The reaction of polyfluoroaromatic compounds with BrF_3 in the absence of Br_2 is sluggish and in the case of hexafluorobenzene little reaction occurs, although from pentafluorobenzene the major product was bromopenta-fluorobenzene.

Reaction of Per-fluoroaromatic Compounds with ClF_3 - Summary

It has been established in these reactions that chlorine is formed in the oxidation of perfluoro alkyl and aryl iodides. The amount of chlorination of the perfluorophenyliodine (V) tetrafluoride depends on the excess of ClF_3 added. It is reasonable, then, to propose that it is a ClF_3/Cl_2 mixture which chlorinates and fluorinates the aromatic ring, but fluorination and possibly chlorination occurs when excess ClF_3 is added to $C_6F_5IF_4$. The chlorine in this case may result from trace impurities in the ClF_3. The mass spectral evidence suggests a maximum of two chlorines are added to the benzene by replacing two fluorine atoms. This would appear to be a similar result to that obtained when excess BrF_3/Br_2 produces a tribromo compound from a mono-bromo compound. The precise position of the

chlorine atoms in the products from C_6F_5I and ClF_3 cannot be ascertained but as there is a maximum of two this would suggest either the chlorine is positioned at either the <u>meta</u> or <u>ortho</u> positions and as the <u>ortho</u> positions are strictly hindered by the IF_4 this may favour position <u>meta</u> to the IF_4 group. However, from mass spectral evidence, the major products obtained when $C_6F_5IF_4$ is reacted with excess ClF_3 are those in which addition of fluorine to the ring, and not chlorine, occurs, suggesting that Cl_2 acts as a catalyst in the reaction. Pedler and his co-workers [102] conclude that fluorination and bromination take place by an electrophilic mechanism. It seems reasonable to postulate a similar mechanism here. Usually nucleophilic attack on substituted pentafluorobenzenes yields only <u>para</u> disubstituted products [103]. The nature of the electrophile in these reactions has not been established but initial attack on the ring may invoke a mechanism whereby the lone pairs of fluorine participate; for example:



E = electrophilic species

Similar participation by the lone pair on iodine would involve electrophilic substitution at the <u>ortho</u> position. The electrophilic centre which is attacked may be the chlorine atom of ClF_3 or the chlorine atoms in Cl_2, made electrophilic by complexing the Cl_2 with ClF_3. Another possible electrophile could be ClF formed in catalytic amounts from the reaction of Cl_2 with the trifluoride. The reaction of chlorine with chlorine trifluoride is known to produce chlorine monofluoride at 250 - 350°C [1].

From the available evidence, the iodine atom of C_6F_5I is oxidatively fluorinated before the ring is attacked, whereas in C_6F_5Br attack on the ring precedes oxidation of the bromine and indeed, under the reaction conditions, no oxidative fluorination of bromine occurs. There is no evidence for ring chlorination of $C_6F_4I_2$ and the evidence in the mass spectrum for ring fluorination can be interpreted in terms of other processes. Iodine, because of its greater size and lower ionization potential, is more easily oxidised to the five valent state than bromine. Bromine is more electronegative than iodine, but the electronegativity of the iodine is increased when it is present as IF_4. It may be this increase in electronegativity of the iodine which facilitates attack on the ring. The aromatic ring of $F_4I\ C_6F_4\ IF_4$ is not attacked. It seems likely that this may be due to steric effects of the bulky IF_4 groups, but it is also noteworthy that this molecule has no <u>para</u> fluorine atom, and this may be evidence that the <u>para</u> fluorine is involved in the reaction mechanism.

<u>The Reaction of Heptafluoro-n-propyl Bromide with Chlorine Trifluoride</u>

ClF_3 does not react with $n\text{-}C_3F_7Br$. No oxidative fluorination of the bromine takes place as is expected from the reaction between C_6F_5Br and ClF_3.

<u>The Reaction of Monofluoro-n-butyl Iodide with Trifluoromethyl Hypofluorite</u>

CF_3OF reacts with $n\text{-}C_4F_9I$ to produce COF_2. The doublet (δ -12·8 p.p.m.) in the ^{19}F n.m.r. spectrum of the reaction product is assigned to IF_5. The peak at δ -7·1 p.p.m. cannot be assigned but it is in the region of mono substituted IF_5 derivatives. Signals at δ -60·3, -87·5 and -127·1 p.p.m. are consistent with fluorocarbon although specific assignments are not possible.

Signals at higher applied fields may be due to I F resonances of I(III) compounds. From this reaction it cannot be discerned whether the IF_5 arises due to cleavage of the C-I bond with CF_3OF or results from decomposition of one or more of the products formed

IV. Reactions of R_FIF_4

CF_3IF_4 with Arsenic Pentafluoride

CF_3IF_4 decomposes at -78°C in the presence of AsF_5 to produce CF_4 and a red-brown solid. No CF_3I was detected and no carbon was detected in the solid product. The ^{19}F n.m.r. spectrum gives no indication as to the constitution of the solid formed but a band at 710 cm^{-1} in the infrared is indicative of an AsF_6^- group [104]. The solid also contains iodine and gives a green solution in IF_5. It may be that the solid is the previously reported $IF_3.AsF_5$ or a decomposition product thereof. AsF_5 is a strong fluoride ion acceptor and it appears that removal of F^- from CF_3IF_4 results in decomposition of the molecule.

CF_3IF_4 and $C_2F_5IF_4$ with Hexafluoropropene

CF_3IF_4 reacts with $CF_3CF{:}CF_2$ to produce heptafluoroisopropyl iodide characterised as C_3F_7I by its mass spectrum ($^m/e$, 246) and distinguished from n-C_3F_7I by its infrared spectrum [105]. The ^{19}F n.m.r. spectra of the reaction mixture is too complicated in the fluorocarbon region to identify minor components. $CF_3CF{:}CF_2$ predominates but the slow disappearance of the IF_4 group can be followed and it cannot be detected after four days. No CF_3I was detected in these reactions. The reaction of $C_2F_5IF_4$ with $CF_3CF{:}CF_2$ also produces $(CF_3)_2$ CFI but more slowly. IF_5 is produced in the reaction of $C_2F_5IF_4$ with $CF_3CF{:}CF_2$, probably from decomposition of the tetrafluoride.

The action of u.v. light on the reaction mixture does not appear to accelerate the formation of $(CF_3)_2$ CFI, implying that

TABLE 13

^{19}F chemical shifts of CF_3IF_4 and CF_3IF_2 in organic solvents (p.p.m.)

Solvent	CCl_3F reference	δ_{CF_3}	δ_{IF_4}	δ_{IF_2}	$\delta_{CF_3} - \delta_{IF_n}$
CCl_3F	int.	-56·1	-32·4		23·7
CCl_3F	int.	-55·4 -28·0	-30·4	-173·5	25·0 -145·5
CH_3CN	int.	-57·6	-35·6		22·0
C_5H_5N	ext.	-57·7 -36·0	-30·0	-174·5	27·7 -138·5
$CH_3CN/C_4H_8O_2$	int.	-57·3	-34·4		22·9
$C_4H_8O_2$	ext.	-60·2	-36·2		24·0

the reaction does not proceed via a radical mechanism. A mixture of IF_5 and I_2 is known to act as an effective source of "IF" and on reaction with $CF_3CF{:}CF_2$ yield exclusively $(CF_3)_2CFI$ [40]. The mechanism of the reaction has been explained as formation of IF in the equilibrium,

$$IF_5 + 2I_2 \rightleftharpoons 5IF$$

$$I\text{-}F + CF_2 = CF\cdot CF_3 \longrightarrow CF_3\cdot CFI\cdot CF_3$$

and subsequent addition of the monofluoride across the double bond. It has been shown that nucleophilic addition to fluoro-olefins occurs very easily and that olefins containing a terminal difluoromethylene group are most reactive [114], the nucleophile invariably becoming attached to the difluoromethylene group. An alternative mechanism has been suggested to explain the addition of "IF" across olefinic double bonds. Sartori and Lehnen [40(b)] state that addition of "IF" involves first addition of iodine across the olefinic bond followed by substitution of one iodine by a fluorine atom.

The Behaviour of CF_3IF_4 in Organic Solvents

CF_3IF_4 is freely soluble in acetonitrile, pyridine and 1, 4 dioxan. Table 13 lists the chemical shifts of CF_3IF_4 in the various solvents with CF_3IF_4 in CCl_3F as a standard. The chemical shifts cannot be compared in every case as sometimes external CCl_3F was used as a reference. Therefore, Table 13 also lists the differences between the chemical shift of the CF_3 group and that of the IF_4 or IF_2 group.

In acetonitrile both signals attributable to CF_3IF_4 are considerably broadened. Although coupling can be observed on the IF_4 signal (J = 17Hz), no coupling is seen on the CF_3 resonance. The chemical shift difference $\delta\ CF_3 - \delta\ IF_4$ of 22·0 p.p.m, 1·7 p.p.m..

less than for CF_3IF_4 in CCl_3F is mainly caused by the upfield shift of 3·2 p.p.m. of the IF_4 group. $\delta(CF_3)$ moves to higher field by only 1·5 p.p.m.

The ^{19}F n.m.r. of CF_3IF_4/CF_3IF_2 mixture in pyridine shows several differences from the spectrum of the same mixture in CCl_3F. No F-C-I-F coupling is observable on the signals due to CF_3IF_4 but the F-F coupling on CF_3IF_2 is still apparent (J = 7Hz). The chemical shift difference between the two signals due to CF_3IF_4 has been reduced by 2·7 p.p.m. mainly due to the downfield shift of the CF_3 resonance whereas the signals due to CF_3IF_2 have moved closer by 7·0 p.p.m. mainly due to an upfield shift of the CF_3 group of 8 p.p.m. The large change in the chemical shift difference of CF_3IF_2 and the retention of coupling may indicate that a complex is formed in solution. Schmeisser and his co-workers [106] have recently reported that CF_3IF_2 forms 1:1 complexes with organic N-bases like pyridine and quinoline. They propose the following structure for the complex,

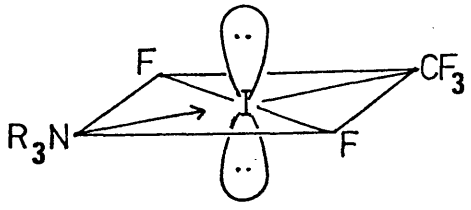


Fig. 7

where the base is <u>trans</u> to a CF_3 group in a square planar configuration, the lone pairs occupying the remaining axial positions. Such a structure preserves the equivalence of the F ligands relative to CF_3. The <u>trans</u> effect of the pyridine may cause the large change in chemical shift of the CF_3 group. This square planar configuration is consistent with the structure proposed for IF_4^- [30].

The collapse or partial collapse of coupling in both CH_3CN and C_5H_5N suggests that these bases promote exchange of fluorine ligands and that the rate of exchange in pyridine is greater than in

acetonitrile. IF_5 in pyridine resonates as a single sharp peak at δ + 22·1 p.p.m. This is readily explained by invoking a fluorine exchange process. The chemical shift above is the weighted mean of the chemical shifts of the axial and equatorial fluorines. In view of the relative bond strengths of C-F and I-F, it seems reasonable to propose exchange of iodine fluorine ligands. The exchange process can then be rationalised as follows:

$$CF_3IF_4 + \text{base} \rightleftharpoons [CF_3IF_3 \cdot \text{base}]^+ + F^-.$$

The mechanism need not be totally ionic but the presence of base might promote association <u>via</u> fluorine bridges by making polarisation of the I-F bond a more favourable process. The intermediate could then be formulated as

$$CF_3F_3\overset{\delta+}{I} \cdots \overset{\delta-}{F} \cdots\cdots IF_4CF_3$$
$$\uparrow$$
$$\text{base}$$

In this rationalisation of the mechanism, the base is co-ordinating to the iodine atom. Pyridine, being a stronger base than acetonitrile, should increase the rate of exchange, as is observed. At this point, it is worth remarking that the ^{19}F n.m.r. spectra of the mixtures $F_4ICF_2CF_2IF_4/F_2ICF_2CF_2IF_2$ and $SF_5CF_2CF_2IF_2/SF_5CF_2CF_2IF_4$ and of $SF_5(CF_2CF_2)_2IF_4$ which were run in CH_3CN solution display the expected coupling without collapse of the signals.

There is no n.m.r. evidence for interaction in dioxan solution. Although the chemical shifts of CF_3IF_4 in dioxan vary, there is no significant change in the chemical shift difference observed in dioxan and only a slight difference when the dioxan is mixed with acetonitrile. The white solid isolated from dioxan solution is thought to be a molecular complex similar to the IF_5 dioxan complex previously reported [31]. Dioxan, being a weaker donor than CH_3CN or C_5H_5N, will not as readily promote exchange of fluorines but may

stabilise CF_3IF_4 for steric reasons. The complex slowly decomposes to give CF_4, CF_3I and I_2 among the decomposition products.

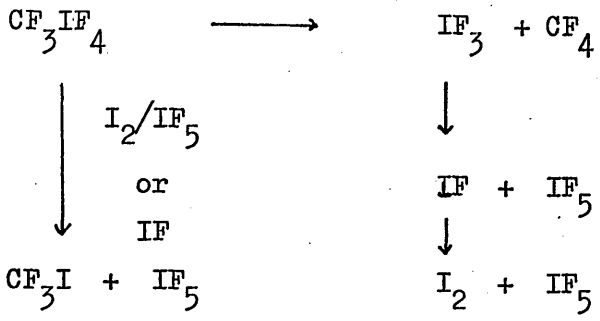
Decomposition and Stability of Perfluoroalkyl and -aryl Tetrafluorides

The stability of R_FIF_4 with respect to decomposition at 20°C is, in order of increasing stability:

$$CF_3- < C_2F_5- < C_4F_9- < (CF_3)_2CF- \quad , \quad SF_5(CF_2CF_2)_2- \quad , \quad C_6F_5-IF_4$$

The stabilities of those compounds not isolated as pure tetrafluorides are not included as the perfluoroalkyliodine(III)difluorides are less stable than the corresponding tetrafluorides. In particular CF_3IF_2 cannot be isolated at room temperature and a mixture of CF_3IF_4 and CF_3IF_2 begins to decompose after a few minutes at 20°C whereas a sample of pure CF_3IF_4 is stable for several hours at 20°C. This suggests that the I(V) tetrafluorides are more stable than the I(III) derivatives in contrast to previous work [64]. $C_2F_5IF_4$ is stable for at least twelve hours and $n\text{-}C_4F_9IF_4$ is stable for several days at 20°C. No decomposition of the last three members of the above series was observed over two weeks either in the solid state or in solution, and $SF_5(CF_2CF_2)_2IF_4$ is stable up to 140°C.

The detectable decomposition products are R_FF, R_FI, IF_5, I_2 and the other product is tentatively formulated as IF_3. No higher or lower homologues are identified, contrary to previous observations, and the application of u.v. light to solutions of R_FIF_4 in CCl_3F does not noticeably accelerate the decomposition. Specifically, the decomposition products from CF_3IF_4 have been identified as CF_4, CF_3I and IF_5 by n.m.r., infrared and mass spectrometry. A peak in the n.m.r. spectrum, which disappears with time, at δ-165 p.p.m. is assigned to the species IF_3. The decomposition is rationalised by the following scheme:



That all the derivatives, R_FIF_4, do not decompose at the same rate, suggests the mechanism of decomposition is not simply intramolecular fluorine transfer from iodine to carbon with subsequent reduction of the iodine. The formation of CF_4 and IF_3 can then most simply be explained by an intermolecular fluorine transfer process facilitated by association of CF_3IF_4 molecules. Evidence for the association of IF_5 molecules in the condensed phases <u>via</u> weak fluorine bridges, has been mentioned previously. If similar interactions are present in the solid state and in solutions of CF_3IF_4, steric crowding and F-F repulsions around the pseudo seven co-ordinate iodine could be relieved by a fluorine transfer process.

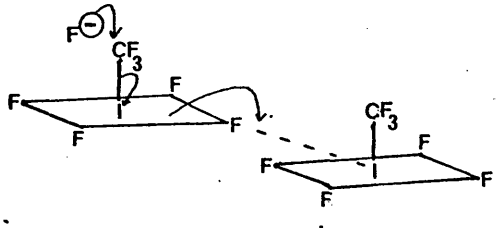


Fig. 8

Intermolecular nucleophilic attack of fluorine on CF_3 would produce CF_4, IF_3, $CF_3IF_5^-$ or CF_3IF_4 and F^-. This associative mechanism need not involve only two CF_3IF_4 molecules but a chain of such interactions may be involved, in which only in the end molecules are fluorine transfers occurring. An interaction similar to that outlined above can be visualised as a possible intermediate in the reaction of CF_3IF_4 with AsF_5 to produce CF_4 and an AsF_6^- complex as the identifiable products. Also, the presence of bases such as pyridine

and acetonitrile may accelerate the formation of such fluorine bridges resulting in the fast intermolecular exchange previously described.

IF_3 is known to disproportionate below 20°C to give I_2 and IF_5, IF being a possible intermediate [41]. The presence of CF_3I as a decomposition product can be accounted for by a series of successive fluorine transfers from CF_3IF_4 to other species, or by C-I bond cleavage with IF formed from the decomposition of IF_3. The latter route is considered more consistent with experimental evidence. It explains the catalytic effect of I_2 and IF_5 on the decomposition and it is analogous to the reaction of CF_3IF_4 with hexafluoropropene to give $(CF_3)_2$ CFI. A series of successive I-F bond cleavage reactions involving CF_3IF_4 would produce CF_3IF_2 as an intermediate, which is not observed. The decomposition of CF_3IF_2 is similarly envisaged with CF_4 and IF as initial products.

The stability of R_FIF_4 increases with the size of the R_F group, the longer the alkyl chain the more stable the tetrafluoride and the stability also increases with the degree of branching of the α carbon atom. It is thought that bulky groups bound to polyvalent iodine cause steric retardation of S_N2 processes of decomposition [75]. In the proposed mechanism of decomposition of R_FIF_4 association increases the co-ordination around iodine. The presence of a bulky R_F group bound to iodine would, therefore, be expected to hinder any such process. The presence of an SF_5 group confers stability on R_FIF_4. The $SF_5CF_2CF_2IF_4/SF_5CF_2CF_2IF_2$ mixture is stable at 20°C for several weeks and it is particularly remarkable that $SF_5(CF_2CF_2)_2IF_4$ can be sublimed at 140°C without decomposition. The stability of R_FSF_5 compounds is well known [107]. The stability of polyvalent iodine attached to aryl ligands is well established. This stability

is probably the result of both the steric and resonance effects of this group making the iodine less susceptible to nucleophilic attack.

Conclusions

ClF_3 oxidises R_FI, where R_F = alkyl or aryl, quantitatively to the corresponding I(III) difluoride or I(V) tetrafluoride under carefully controlled conditions. There is no evidence to suggest that under similar conditions perfluoroalkyl or aryl bromides can be similarly oxidised, but ClF_3 can add chlorine and fluorine to a pentafluorophenyl ring, such that the ring becomes olefinic or alicyclic. These additions may only occur in the presence of chlorine.

Spectroscopic evidence suggests that R_FIF_4 possesses C_{4v} symmetry, the R_F being situated in the apical position of a tetragonal pyramid, and with free rotation of R_F around the C-I bond.

Perfluoroalkyliodine (V) tetrafluorides are more stable than had been supposed [14]. The stability of these compounds with respect to decomposition appears to depend on the size of the R_F group. CF_3IF_4 reacts with AsF_5 to produce CF_4 and an unidentified compound containing the AsF_6^- ion. It also acts as a source of "IF" to $CF_3CF{:}CF_2$ to produce CF_3CFICF_3. The reactions of CF_3IF_4 can be interpreted on the basis of association via I-F ... I bridges in the condensed phases.

EXPERIMENTAL

Apparatus: Figure 9 illustrates the monel metal vacuum line used for transfer of chlorine trifluoride. It was constructed from standard couplings and valves (Autoclave Engineers) and a monel Bourdon Gauge (Helicoid). Reactions involving ClF_3 were carried out in Kel-F traps (Argonne Natural Laboratory) and attached to the line via Hoke diaphragm valves. The line was calibrated with CO_2 and both line and traps were well seasoned with ClF_3 before use.

Chemicals: Reagents were obtained from sources indicated in Table 14. Infrared and n.m.r. references are included. The volatile iodides were purified by trap to trap distillation. C_6F_{14} and C_6F_6 were purified by trap to trap distillation and stored over Na. CCl_3F, CH_3CN, dioxan and pyridine were stored over Linde 4A molecular sieves. Other reagents were used without further purification.

Experimental Procedure for Oxidation of Perfluoroalkyl/aryl iodides with ClF_3

ClF_3 was added in small portions to a weighed amount of perfluoroalkyl/aryl halide in perfluoro-n-hexane at -78°C. The course of the reaction depended greatly on the amount of solvent and the speed of addition of ClF_3. The mixture was allowed to warm overnight (14 hours) and the final reaction temperature recorded. At this temperature the volatile products, mainly chlorine, and some solvent were removed through the waste system (Fig. 9) and not further investigated. The reaction mixture was transferred to a conventional pyrex vacuum system. The involatile polyfluorides were isolated by removing solvent at 20°C. The volatile polyfluorides were condensed on to NaF and isolated by fractional distillation of 0°C.

In the case of the more volatile R_FI compounds, several reaction stoicheimetries were tried to obtain ideal reaction conditions. Other reactions were investigated without varying experimental conditions.

MONEL METAL VACUUM LINE

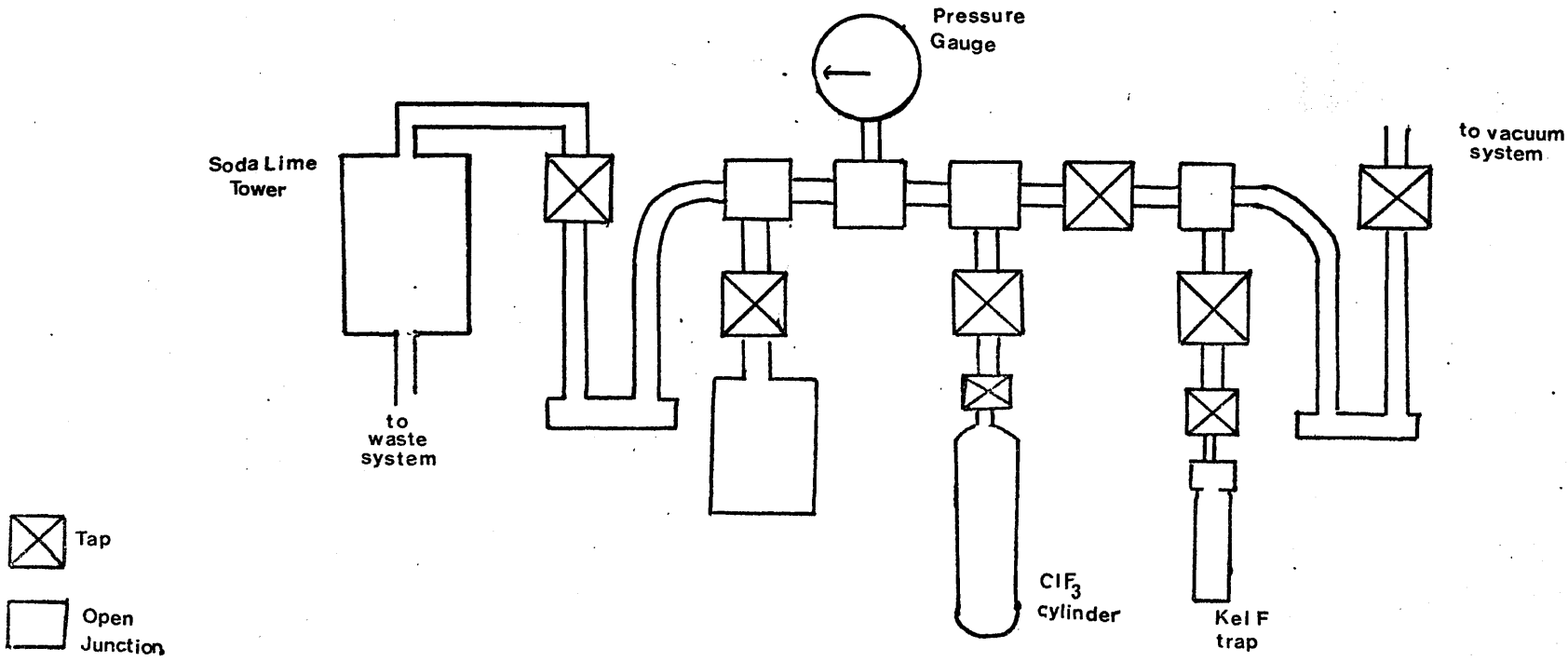


TABLE 14

Compound	Source	I.R.	N.M.R.
CF_3I	Fluorochem Ltd.	88	82
C_2F_5I	" "	108	
$(CF_3)_2CFI$	" "	105	82
$n\text{-}C_4F_9I$	" "		64
ICF_2CF_2I	" "		
$SF_5CF_2CF_2I$	Gifts from Dr. J.Hutchinson I.C.I. Mond Division		
$SF_5(CF_2CF_2)_2I$			
C_6F_5I	Fluorochem Ltd.	99	97
IC_6F_4I	" "		
C_6F_5Br	Imperial Smelting Corpn.	99	97
C_3F_7Br	Fluorochem Ltd.	109	
ClF_3	Matheson	1	1
CF_3OF	Peninsular Chem Research	109	82
$n\text{-}C_6F_{14}$	Fluorochem Ltd.	109	
CCl_3F	B.D.H.	110	
CH_3CN	"	112	
Pyridine	"	112	
1, 4 dioxan	"	112	
AsF_5	Peninsular Chem Research	104	81
$CF_3CF{:}CF_2$	" "	109	
C_6F_6	Fluorochem Ltd.	111	80
IF_5	" "	6, 7	10

I. Preparation of Perfluoroalkyliodine (V) Tetrafluorides

Reactions of Trifluoromethyl Iodide with Chlorine Trifluoride.

(a)	CF_3I (m.mol)	ClF_3 (m.mol)	C_6F_{14} (g)	final reaction temperature	Identified Products.
(i)	7.41	10.38	3.21	-78°C	CF_4
(ii)	6.13	11.61	3.61	-78°C	CF_3I SiF_4 I_2

The volatile products were identified by their infrared and mass spectra. Addition of ClF_3 was accompanied by an initial pressure rise caused by an exothermic reaction. No identifiable iodine polyfluorides could be isolated in these reactions.

(b)	CF_3I (m.mol)	ClF_3 (m.mol)	C_6F_{14} (g)	final reaction temperature	Identified Products.
(i)	6.42	9.62	3.76	-70°C	CF_3IF_4 CF_3IF_2 IF_5 (trace) I_2 (trace)
(ii)	5.01	8.73	4.58	-50°C	CF_3IF_4 CF_3IF_2
(iii)	5.62	2.41	3.6	-73°C	CF_4 CF_3I I_2 IF_5

In reaction (iii) a white solid which decomposed rapidly above 0°C was observed. CF_3IF_2 was not isolated. In reaction (i) approximately equal amounts of trifluoromethyliodine (V) tetrafluoride and trifluoromethyliodine (III) difluoride were obtained. The ratio CF_3IF_4 : CF_3IF_2 in reaction (ii) was approximately 6:1, based on ^{19}F n.m.r. signal intensities. The mixtures were isolated as white solids which decomposed to liquids on standing. A ^{19}F n.m.r. spectrum of a solution of the mixture in CCl_3F contained peaks at (a) δ -28.8 p.p.m. (triplet, J_{FF}=8 Hz); (b) δ -30.4 p.p.m, (quartet, J=18Hz); (c) δ -55.7 p.p.m. (quintet, J=18 Hz); (d) δ -172.7 p.p.m.

(quartet, J 8Hz). Signals (a) and (b) were attributed to CF_3IF_2 and (b) and (c) to CF_3IF_4. Infrared spectrum (vapour phase, < 6mm, 4000-400 cm^{-1}) of 1:1 mixture: 1348m, 1265vs, 1229s, 1182s, 1155m, 1122w, 1116w, 1101sh, 1072vs, 1028m, 858m, 818w, 794w, 775w, 762sh, 759m, 748m, 741sh, 710m, 700sh, 636s, 600s, 535w, cm^{-1}.

(c)	CF_3I (m mol)	ClF_3 (m mol)	C_6F_{14} (g)	final reaction temperature	Identified Products
	5·68	8·86	3·37	-60°C	CF_3IF_4, IF_5, CF_4, CF_3I } (trace)
	4·59	9·11	5·21	-42°C	CF_3IF_4

Trifluoromethyliodine (V) tetrafluoride was isolated as a white, moisture sensitive solid, readily volatile at 20°C and soluble in CCl_3F. It was characterised by its ^{19}F n.m.r. spectral parameters (Table 1 and 2). The gas infrared and solid Raman spectra were recorded (Table 4). The mass spectra at 70 eV (Table 5.1) and 20eV were independent of source temperature in the range 130-210°C. Mass spectrum (20eV): $^m/_e$ 215 (< 0·5), CF_3IF^+; 203(14), IF_4^+; 196(66), CF_3I^+; 184(4), IF_3^+; 177(3), CF_2I^+; 165(22), IF_2^+; 146(3), IF^+; 127(12), I^+; 88(3), CF_4^+; 69(100), CF_3^+; 50(< 0·5), CF_2^+; 31(< 0.5) CF^+.

Reaction of Pentafluoroethyl Iodide with Chlorine Trifluoride

	C_2F_5I (m mol)	ClF_3 (m mol)	C_6F_{14} (g)	final reaction temperature	Identified Products
(i)	3·60	6·84	3·06	-35°C	$C_2F_5IF_4$, IF_5 (trace)
(ii)	6·18	10·40	5·76	13°C	$C_2F_5IF_4$, C_2F_6, IF_5 } (trace)
(iii)	3·70	8·61	3·12	-30°C	$C_2F_5IF_4$

Products (i) and (ii) were isolated as liquids. C_2F_6 was identified by its infrared spectrum[109] and IF_5 by its i.r. and ^{19}F n.m.r. spectra. In (i) ClF_3 was not added gradually and in (ii) the mixture was allowed to warm to too high a temperature. In (iii) pentafluoroethyliodine (V) tetrafluoride was isolated as a white solid, volatile at 20°C and soluble in CCl_3F. ^{19}F n.m.r. spectral parameters are listed in Tables 1 and 2. Infrared spectrum (vapour phase, < 3mm, 4000-400 cm^{-1}): 1321m, 1264s, 1224s, 1160vw, 1131m, 1118sh, 1084w, 1080sh, 919m, 842m, 751sh, 749m, 732m, 647w, 600 cm^{-1}.

Infrared spectrum, product (i) (liquid film): 1450vw, 1320s, 1265sh, 1225vs. br, 1122s, 1063sh, 1024sh, 975w, 948sh, 900s, 887sh, 760sh, 741s, 730sh, 696s, 651sh, 650-480s, vbr, cm^{-1}. Infrared spectrum, product (ii) (vapour phase, < 3mm, 4000-400 cm^{-1}): 1355sh, 1321s, 1240vs br, 1189sh, 1151m, 1133sh, 1120s, 1115s, 1107sh, 1073w, 989w, 958w, 918s, 855w, 816w, 791w, 747sh, 729s, 708s, 642vs, 598vs, 588sh, 534w, cm^{-1}.

The mass spectrum of product (ii) was recorded at 70eV (Table 5.2.), 20eV and 12eV. No fragmentation was observed at 12eV.

Mass spectrum (20eV): $^m/_e$ 265(1), $C_2F_5IF^+$; 254(83), I_2^+; 246(88), $C_2F_5I^+$; 227(3), $C_2F_4I^+$; 215(0·5), CF_3IF^+; 203(15), IF_4^+; 196(1), CF_3I^+; 184(7), IF_3^+; 177(3), CF_2I^+; 165(20), IF_2^+; 146(4), IF^+; 127(21), I^+; 119(100), $C_2F_5^+$; 100(4), $C_2F_4^+$; 81(1), $C_2F_3^+$; 69(24), CF_3^+; 51(1), CF_2^+; 31(2), CF^+.

Reaction of Heptafluoroisopropyl Iodide with Chlorine Trifluoride

	$(CF_3)_2CFI$ (m mol)	ClF_3 (m mol)	C_6F_{14} (g)	final reaction temperature	Identified Products
(i)	5·92	8·85	3·66	-30°C	$(CF_3)_2CFIF_4$
(ii)	7·73	10·89	5·70	-20°C	$(CF_3)_2CFIF_4$

Heptafluoroisopropyliodine (V) tetrafluoride [Found: C, 9·6; F, 56·4; I, 34·0% $C_3F_{11}I$ requires C, 9·7; F, 56·2; I, 34·1%] was isolated as a

white moisture sensitive solid, m p. 48 ± 4°C. It sublimed slowly at 20°C and was soluble in CCl_3F. Its ^{19}F n.m.r. spectrum in CCl_3F (Tables 1 and 2) and mass spectrum at 70eV (Table 5, 3.) were recorded.

Infrared spectrum (nujol and fluorolube mulls, 4000-400 cm^{-1}): 1538w, 1340sh, 1284s br, 1247vs, 1226vs, 1158sh, 1067 m.br, 959s, 884s, 855s, 746s, 716sh, 710s, 676w, 665w, 614sh, 596-480 s br, cm^{-1}.

Reaction of Nonafluoro-n-butyl Iodide with Chlorine Trifluoride

	C_4F_9I (m mol)	ClF_3 (m mol)	C_6F_{14} (g)	final reaction temperature	Identified Products.
(i)	3·17	6·32	5·59	-60°C	$C_4F_9IF_4$ $C_4F_9IF_2$
(ii)	4·94	11·14	2·47	-50°C	Decomposition products.
(iii)	4·89	10.54	2·79	-78°C	Explosion destroyed reaction vessel
(iv)	4·31	8·10	4.19	-60°C	$C_4F_9IF_4$ IF_5 (trace)
(v)	6·27	9·62	6·69	20°C	$C_4F_9IF_4$ IF_5 (trace)

Nonafluoro-n-butyliodine (V) tetrafluoride was isolated as a colourless liquid which distils slowly at 20°C. In reaction (ii), decomposition products only were isolated (I_2, C_4F_{10}, SiF_4) in a glass ampoule. Possibly too little solvent was used. In reaction (iii), the violent reaction may have resulted from a combination of too little solvent and rapid addition of ClF_3. $C_4F_9IF_4$ was characterised by its ^{19}F n.m.r. spectrum (Tables 1 and 2), mass spectrum at 70eV (Table 5, 4) and its infrared spectrum.

Infrared spectrum (liquid film, 4000-400 cm^{-1}): 1353sh, 1348s, 1240br.s, 1217s, 1197sh, 1149s, 1111m, 1099m 1022w, 991m, 950w, 916w, 899 vw, 855w, 835w, 789m, 774m, 745sh, 718s, 689s, 648sh, 640m, 591s.br, 539s, cm^{-1}.

Reaction of 1, 2 Diiodotetrafluoroethane with Chlorine Trifluoride

	ICF_2CF_2I (m mol)	ClF_3 (m mol)	C_6F_{14} (g)	final reaction temperature	Identified Products.
(i)	3·49	11·14	3·0	-35°C	R_FIF_4
					IF_5
(ii)	3·63	12·78	4·3	-35°C	$F_4ICF_2CF_2IF_4$
					$F_2ICF_2CF_2IF_2$
					IF_5
					IF_3

The diiodotetrafluoroethane contained substantial amounts of I_2. A bulky white solid, which decomposed on melting at 65-67°C, was isolated. It was soluble in IF_5 and CH_3CN but only sparingly soluble in CCl_3F. The solid from (ii) was characterised from its ^{19}F n.m.r. spectrum in CH_3CN (Tables 1 and 2) and its mass spectrum at 70eV (Table 5, 5.). The product from reaction (i) contained an IF_4 group from its ^{19}F n.m.r. spectrum in CCl_3F. Decomposition was detected after four days, C_2F_5I and I_2 being among the products. Infrared spectrum (nujol and fluorolube mulls, 4000-400 cm^{-1}): 1252s, 1231s, 1222sh, 1144s, 1132sh, 913w, 709m, 695m, 591m, 564m, 558sh, 524m, 518sh, 507m, 478s, cm^{-1}.

II. Oxidation of Perfluoroalkylsulphur (VI) Pentafluorides by ClF_3

Reaction of 1-Iodo - 2-Sulphur (Vl) Pentafluoride-tetrafluoroethane with Chlorine Trifluoride.

ClF_3 (0·63g, 6·84 m mol) was added slowly to $SF_5CF_2CF_2I$ (1·56g, 4·41 m mol) in C_6F_{14} (3·34g) at -65°C. A white solid precipitated at this temperature. The reaction was allowed to warm to -30°C overnight. A bulky white solid, m p. 69-72°C, slightly volatile at 20°C was isolated.

Elemental analysis. Found: C, 5·8; F, 57·2; I, 29·9; S, 7·5%. $C_2F_{13}IS$ requires C, 5·6; F, 57·4; I, 29·6; S, 7·5%. Although a

pure compound is indicated from the analysis, its ^{19}F n.m.r. spectrum (Table 6 a) shows it to be a mixture of 1-iodine (V) tetrafluoride - 2-sulphur (Vl) pentafluoride - tetrafluoroethane and 1-iodine (III) difluoride - 2-sulphur (Vl) pentafluoride - tetrafluoroethane.

Infrared spectrum (nujol and fluorolube mulls, 4000-400 cm^{-1}): 1325vw, 1370sh, 1232s, 1152s, 901sh, 872s, 722s, 676s, 602s, 585s, 528m, 425sh, 417w.

Mass spectrum (70eV): $^{m}/e$ 373 (0·1), $SF_5C_2F_4IF^+$; 354(1) $SF_5C_2F_4I^+$; 254(4) I_2^+; 246(1), $C_2F_5I^+$, $SF_5C_2F_5^+$; 227(12), $C_2F_4I^+$, $SF_5C_2F_4^+$; 208(2) $C_2F_8S^+$, $C_2F_3I^+$; 203(2), IF_4^+; 196(0·1), CF_8S^+, CF_3I^+; 189(0·2), $C_2F_7S^+$, $C_2F_2I^+$; 184(2), IF_3^+; 181(0·3), IOF_2^+; 177(10), CF_7S^+, CF_2I^+; 170(0·3), $C_2F_6S^+$, C_2FI^+; 165(10), IF_2^+; 158(3) CF_6S^+, CFI^+; 151(0·1), $C_2F_5S^+$, C_2I^+; 146(11), IF^+; 139(1), CF_5S^+, CI^+; 127(74), SF_5^+, I^+; 120(1), CF_4S^+; 119(55), $C_2F_5^+$; 113(0·2), $C_2F_3S^+$; 108(1), SF_4^+; 101(2), CF_3S^+; 100(41), $C_2F_4^+$; 89(100), SF_3^+; 82(1), CF_2S^+; 81(10), $C_2F_3^+$; 70(44), SF_2^+; 69(43), CF_3^+; 51(2), SF^+; 50(23), CF_2^+; 31(6), CF^+.

Reaction of 1-Iodo - 4-sulphur (Vl) Pentafluoride-octafluorobutane with Chlorine Trifluoride.

ClF_3(0·70g, 7·60 m mol.) was added gradually over thirty minutes to $SF_5(CF_2CF_2)_2I$ (1·67g, 3·67 m mol.) in C_6F_{14} (3.92g) at -78°C. The mixture was allowed to warm to -36°C overnight. A bulky white solid, m p. 66-68°C, soluble in CH_3CN was isolated at 20°C. The solid was stable to 140°C without decomposition. It was characterised by analysis (Found: C, 8·9; F, 60·5; I, 24·3; S, 6·2%. $C_4F_{17}IS$ requires C, 9·1; F, 60·9; I, 23·9, S, 6·1%), and by its ^{19}F n.m.r. spectrum (Table 6, b.) as 1-iodine (V) tetrafluoride - 2-sulphur (VI) pentafluoride-octafluorobutane. Trace quantities of the I(III) analogue were indicated from its ^{19}F n.m.r. spectrum.

Infrared spectrum (nujol and fluorolube mulls, 4000-400 cm^{-1}):

1313w, 1227s, 1199sh, 1154s, 1127w, 1068m, 1039w, 917m, 888s, 849m, 769m, 720w, 680m, 650m, 612sh, 592s, 571s, 534s, cm^{-1}:

Raman spectrum (solid, 1550-200 cm^{-1}): 1511(4), 1500(5), 1310(3), 123(3), 1130(2), 1091(2), 1062(2), 1006(2), 919(3), 842(6), 717(12), 686(16), 653(1), 616(3), 560(15), 547(14), 431(2), 414(2), 381(3), 372(3), 274(9) cm^{-1}:

Mass spectrum (70eV). m/e: 473(<0·1), $SF_5(CF_2)_4IF^+$; 454(6), $SF_5(CF_2)_4I^+$; 327(4), $C_4F_{13}S^+$, $C_4F_8I^+$; 308(<0·1), $C_4F_{12}S^+$, $C_4F_7I^+$, $C_4F_7I^+$; 277(0·1), $C_3F_{11}S^+$, $C_3F_6I^+$; 265(0.2), $C_2F_5IF^+$; 258(0·1), $C_3F_{10}S^+$, $C_3F_5I^+$; 254(14), I_2^+; 239(2), $C_3F_9S^+$, $C_3F_4I^+$; 227(2), $C_2F_9S^+$, $C_2F_4I^+$; 220(1), $C_3F_8S^+$, $C_3F_3I^+$; 219(21), $C_4F_9^+$; 213(0·2), $C_4F_7S^+$, $C_4F_2I^+$; 208(2), $C_2F_8S^+$, $C_2F_3I^+$; 203(2), IF_4^+; 201(1), $C_3F_7S^+$, $C_3F_2I^+$; 200(1), $C_4F_8^+$; 196(1), CF_8S^+, CF_3I^+; 189(0.3), $C_2F_7S^+$, $C_2F_2I^+$; 184(2), IF_3^+; 182(0·4), $C_3F_6S^+$, C_3FI^+; 181(7), IOF_2^+, $C_4F_7^+$; 177(8), CF_7S^+, CF_2I^+; 170(0·3), $C_2F_6S^+$, C_2FI^+; 169(2), $C_3F_7^+$; 165(8), IF_2^+; 162(0·4), $C_4F_6^+$; 158(1), CF_6S^+, CFI^+; 150(1), $C_3F_6^+$; 146(3), IF^+; 131(32), $C_3F_5^+$; 127(31), SF_5^+, I^+; 119(18), $C_2F_5^+$; 112(1), $C_3F_4^+$; 108(1), SF_4^+; 100(36), $C_2F_4^+$; 93(5), $C_3F_3^+$; 81(5), $C_2F_3^+$; 74(1), $C_3F_2^+$; 70(5), SF_2^+; 69(100), CF_3^+; 62(1), $C_2F_2^+$; 51(5), SF^+; 50(4), CF_2^+; 43(23), C_2F^+; 31(15), CF^+.

III. Reaction of Perfluoroaromatic Halides with ClF_3

Reaction of Iodopentafluorobenzene with Chlorine Trifluoride

	C_6F_5I (m mol)	ClF_3 (m mol)	excess ClF_3 %	final reaction temperature	Identified Products.
(i)	7·26	11·39	18	-15°C	$C_6F_5IF_4$
(ii)	3.85	7·60	50	20°C	Highly ring chlorinated and fluorinated species
(iii)	2·48	5·06	30	20°C	$C_6F_5IF_4$ + ring chlorinated species.

(iv)	4·09	5·82	5	20°C	$C_6F_5IF_4$ + small amount of ring chlorinated species.
(v)	3·99	5·95	12	25°C	$C_6F_5IF_4$ + small amount of ring chlorinated species.

Approximately 3 ml. C_6F_{14} was employed as solvent in each reaction. Reactions (ii), (iii) and (iv) were performed by Mr. J. Berry during his B.Sc. thesis[101]. The product from reaction (i) was a white crystalline solid, m p. 72-74°C, only slightly volatile at 20°C, which could be recrystallised from CCl_3F. It was identified as pentafluorophenyliodine (V) tetrafluoride by analysis, (Found: C, 20·6; F, 45·2; I, 33·7%. C_6F_9I requires C, 19·5; F, 46·2; I, 34·3%), its ^{19}F n.m.r. spectrum (Table 7) and its mass spectrum (Table 9). Its infrared spectrum (Table 8) was also recorded.

Product (ii) was a colourless viscous liquid at room temperature. Both the infrared and mass spectra closely resembled those for the product obtained when $C_6F_5IF_4$ is reacted with ClF_3, and indicated the presence of ring chlorinated and fluorinated species.

Reaction (iii) yielded a pale green viscous liquid from which a pale yellow "slush" was isolated by pumping on the liquid for one hour. The infrared spectrum of this product contained bands consistent with $C_6F_5IF_4$. The mass spectrum contained a parent ion $^m/_e$ = 370 and ring chlorinated fragments of lower relative intensity than product (ii).

Product (iv) was isolated as a dry hard white solid, m p. 60 $\pm$ 2°C. The ^{19}F n.m.r. spectrum of this solid displayed peaks at δ -7·7 p.p.m. (triplet, J=28Hz); -132 p.p.m. (mult iplet); -162 p.p.m. (mult iplet) consistent with $C_6F_5IF_4$. Its infrared and mass spectra were also consistent with $C_6F_5IF_4$. The Raman spectrum of this solid was recorded (Table 8). Product (v) was isolated as a slightly "mushy"

solid. Its ^{19}F n.m.r. spectrum contained peaks at δ -7·3, -127, -142, -157 p.p.m. consistent with $C_6F_5IF_4$.

Reaction of Pentafluorobenzene Iodine (V) Tetrafluoride with Chlorine Trifluoride

ClF_3 (0·5g, 5·3 m mol) was added to $C_6F_5IF_4$ (product v) (approximately 0·5g, 1·3 m moles) in C_6F_{14} (3 ml.) at -78°C. The reaction mixture was allowed to warm to room temperature over sixteen hours. Chlorine was produced and a colourless viscous liquid was isolated. The ^{19}F n.m.r. spectrum of this liquid (CCl_3F, C_6F_6 internal refs.) contained a doublet δ = + 11·4 p.p.m. (J = 90Hz) assigned to IF_5, a broad peak (width at half-ht.=140 Hz) at δ = - 5·5 p.p.m. and a series of low intensity peaks, the chemical shifts of which could not be accurately determined, at δ = -80, -88, -92, -108, -132, -147, -156 p.p.m. There was also evidence of peaks of even less intensity.

Infrared spectrum (liquid film, 4000-400 cm^{-1}): 1864m, 1780m, 1740w, 1662s, 1634s, 1510sh, 1494s, 1402sh, 1377m, 1359m, 1302s, 1284sh, 1210s.br, 1152s.br, 1096s, 1061s, 1034m, 1005s, 990s, 972s, 946s, 912m, 896sh, 879sh, 867s, 856sh, 844sh, 805m, 798sh, 786w, 763sh, 758m, 715m, 700m, 686m, 665w, 626sh, 600s, 600-400 cm^{-1} broad absorption.

The mass spectrum at 70eV was recorded at a source pressure of 5×10^{-6} torr. (Table 10)

The reaction of 1, 4 Diiodotetrafluorobenzene with Chlorine Trifluoride

ClF_3 (0·72g, 7·85 m mol) was added to $C_6F_4I_2$ (0·92g, 2·29 m mol) in C_6F_{14} (~3 ml.) at -70°C. $C_6F_4I_2$ is insoluble in C_6F_{14}. The mixture appeared to react at -60°C with the production of chlorine. It was allowed to warm overnight to -20°C, and a white solid was isolated. It was insoluble in IF_5, C_6F_6, CH_3CN and CCl_3F. The analysis (Found: C, 14·1; F, 36·6; I, 49·4%. $C_6F_{12}I_2$ requires C, 13·0; F, 41·1; I, 45·9% and $C_6F_8I_2$ requires C, 15·1; F, 31·8; I, 53·1; %) and mass spectrum (Table 11) suggested that the solid was a mixture of

1, 4 - diiodine (V) tetrafluoride tetrafluorobenzene and 1, 4 - diiodine (III) difluoride tetrafluorobenzene.

Infrared spectrum (nujol and fluorolube mulls, 4000-400 cm^{-1}): 1482s, 1311w, 1269w, 1245sh, 1236s, 1167sh, 1153w, 1066w, 1054w, 976s, 968s, 891w, 764sh, 758s, 738sh, 724m, 660vw, 607m, 590s, 571s, 562sh, 525sh, 506s, 476s, 429m, 418w, cm^{-1}

Reaction of Bromopentafluorobenzene with Chlorine Trifluoride

	C_6F_5Br (m mol)	ClF_3 (m mol)	C_6F_{14} (ml)	final reaction temperature	Identified Products.
(i)	6·48	10·39	3	20°C	C_6F_5 Br. C_6F_9 Br.
(ii)	5·96	8·17	3	-36°C	ring chlorinated and fluorinated products.

Products (i) and (ii) were colourless liquids, volatile at 20°C, identified from their ^{19}F n.m.r. and mass spectra (Table 12) as mixtures consisting mainly of unreacted C_6F_5Br. C_6F_9Br. and some ring-fluorinated and-chlorinated compounds were also formed.

^{19}F n.m.r. spectrum (C_6F_6 internal ref.) δ -97·8, -100·5, -105·4, -108·3, -110·6, -114·6, -117·3, -119·4, -132·3, -141·2, -148·9, -149·5, -149·8, -154·0, -156·4, -159·0, -160.1 p.p.m.

Infrared spectrum (liquid film, 4000-400 cm^{-1}): 1595w, 1558sh, 1501s, 1418w, 1364m, 1324s, 1312s, 1303sh, 1189s, 1145s, 1089s, 1078sh, 1056sh, 1043s, 1004s, 976s, 936m, 879s, 876w, 834s, 826m, 798s, 787m, 777w, 769w, 749s, 714w, 690sh, 677w, 655vw, 632m, 616w, 602m, 580w, 557w, 506w, 470w, cm^{-1}.

Infrared spectrum (gas phase, ~ 2 m.m. Hg 4000-400 cm^{-1}): 1508s, 1368w.br, 1315s, 1275w, 1239s, 1222sh, 1194sh, 1153m, 1143sh, 1091s, 1062s, 1047sh, 1002m, 980m, 965s, 940w, 885m, 867w, 836m, 815m, 795sh, 752m, 729m, 696m, 535w, 606w, 487w, 467w, 382sh, cm^{-1}.

IV. Reactions of R_FIF_4

Reaction of CF_3IF_4 with Arsenic Pentafluoride

Excess AsF_5 was condensed on to a sample of CF_3IF_4 (0·5g, 2 m mol), containing trace quantities of CF_3IF_2, in CCl_3F at -196°C. The mixture was quickly warmed to -78°C whereupon a vigorous reaction occurred, producing a red solid, a green liquid and CF_4. The mixture was warmed to 20°C without further reaction. CF_4 and AsF_5 were removed at -80°C leaving a white solid which changed to dark green at 20°C. On pumping at 20°C, a reddish-brown solid was isolated. It contained positive iodine. It formed a dark green solution in IF_5 but no signals, other than those due to solvent, were detected in the ^{19}F n.m.r. spectrum. The ^{19}F n.m.r. spectrum of the solid in CCl_3F contained a strong singlet at δ-7·0 p.p.m. and a weak singlet at δ+143·8 p.p.m. Infrared spectrum of solid (nujol mull, 4000-400 cm^{-1}): 700s, 671sh cm^{-1}. Elemental analysis. Found: C, 0·0 ; F, 27·5; As, 18·3; I, 4·7%. (As:F=1:6).

Reaction of Hexafluoropropene with R_FIF_4

(i) Approximately 0·4g of a mixture of CF_3IF_2 and CF_3IF_4 (product 1(b)(i) was allowed to react with a large excess of $CF_3CF{:}CF_2$ at 20°C for two days. The initial purple colour changed to pale brown after one day. The mixture was separated by fractional distillation at -25, -80, -160 and -196°C and the products identified by infrared and mass spectrometry as CF_4, CF_3I, CF_3CFICF_3 and unreacted $CF_3CF{:}CF_2$.

(ii) A large excess of $CF_3CF{:}CF_2$ was added to CF_3IF_4 (0·6g, 2 m mol) in CCl_3F at -196°C and the mixture allowed to warm quickly to 20°C. The reaction was followed by ^{19}F n.m.r. spectroscopy. Initially the solution was pink. After one day traces of a brown solid precipitated and the solution became colourless. The brown solid could not be isolated but trace quantities of a white solid remained in the flask after removal of the volatiles. A qualitative test indicated this solid contained

positive iodine. The volatiles were identified by infrared and mass spectrometry as CF_4, CF_3I, CF_3CFI_4 and $CF_3CF{:}CF_2$ as before.

(iii) A mixture of excess $CF_3CF{:}CF_2$ and $C_2F_5IF_4$ in CCl_3F remained at 20°C for twelve days. The volatiles were identified as before and the reaction was again followed by ^{19}F n.m.r. spectroscopy. The products were C_2F_5I, IF_5, CF_3CFICF_3 and unreacted $CF_3CF{:}CF_2$. U.v. irradation in (ii) and(iii)had no effect on the reaction rate or products.

Behaviour of CF_3IF_4 in organic solvents.

CF_3IF_4 was dissolved in acetonitrile, pyridine, 1, 4 -dioxan and 1, 3 -dioxan/acetonitrile and the ^{19}F n.m.r. spectra recorded (Table 13). Pyridine and acetonitrile accelerated the rate of decomposition, but CF_3IF_4 is stable in dioxan indefinitely. Unstable white solids were isolated on removing the solvent from the acetonitrile and the dioxan solutions. The sample of CF_3IF_4 dissolved in pyridine contained approximately 15% CF_3IF_2 as impurity.

Decomposition of R_FIF_4

Decomposition of R_FIF_4 was followed in the gas phase by i.r. spectroscopy, in the solid state by monitoring the infrared spectrum of the volatile products and in solution by n.m.r. spectroscopy. Decomposition of impure samples of CF_3IF_4 was detectable within 0·5h, but that of pure samples was much slower, 4 - 5 hrs., the identifiable products being CF_4, CF_3I, IF_5 and I_2.

Hydrolysis of R_FIF_4 Compounds

R_FIF_4 were hydrolysed in water to produce white or pale yellow solids similar to those obtained previously[64] and formulated as impure $(R_F)_2I^+$ compounds. They were not further investigated. CF_3IF_4 on hydrolysis in ethanolic KOH produced CHF_3 and traces of CF_4 and a white solid containing positive I and C-F groups.

V. Other Reactions

Reaction of Heptafluoro-n-propyl Bromide with Chlorine Trifluoride

ClF_3 (0·63g, 6·85 m mol) was added stepwise to C_3F_7Br (0·56g, 2·22 m.mol) in C_6F_{14} (3·1g) at -78°C and the reaction mixture allowed to warm overnight to -35°C over a 14 hr. period. The reaction mixture was purified in the normal way and the products investigated. Its ^{19}F n.m.r. spectrum contained three strong peaks consistent with C_6F_{14}, some peaks of lesser intensity consistent with C_3F_7Br and a broad peak of low intensity at δ + 88 p.p.m. (downfield from external CCl_3F). Both infrared and mass spectrometric evidence were consistent with the presence of C_3F_7Br and C_6F_{14} and possibly some ClF_3.

The Reaction of Nonafluoro-n-butyl Iodide with Trifluoromethyl Hypofluorite

Excess CF_3OF was added to n-C_4F_9I (1·62g, 0·4 m mol) at 196°C and the mixture allowed to warm to -5°C overnight to give a colourless liquid and traces of a white solid. The products volatile at -80°C, CF_3OF and COF_2, were removed and the resulting mixture allowed to stand at 20°C for about 1 hour during which it turned brown and showed signs of decomposition. The liquid was not readily miscible with CCl_3F. A ^{19}F n.m.r. spectrum of the product in CCl_3F contained peaks at δ + 12·8, doublet (J = 94Hz); -7·1, singlet, -87·5, broad singlet; -127·1, complex; -160·5, -171·8, -173·0, -173·9 broad singlets; and -212.3 p.p.m., singlet.

CHAPTER TWO

THE REACTIONS OF IODINE PENTAFLUORIDE WITH SOME ORGANOSILICON COMPOUNDS AND SOME SULPHITE AND PHOSPHITE ESTERS

PREPARATION AND PROPERTIES OF ALKOXOIODINE(V) FLUORIDES

INTRODUCTION

Alkoxo- and aryloxosilanes have been widely used to prepare substituted derivatives of covalent fluorides. With typical Lewis acids, MF_n cleavage of the Si-O bond occurs.

$$MF_n + R_3SiOR' \longrightarrow MF_{n-1}OR' + R_3SiF$$

The fluorination of organosilicon compounds with sulphur tetrafluoride has received some attention. Si-O-Si bridges in siloxanes are cleaved with the formation of Si-F bonds and from silanols and silanediols, fluorosilanes and difluorosilanes, respectively are obtained. Alkoxosilanes yield the corresponding fluorosilane, alkyl fluoride and dialkylsulphite[115].

$$3Me_3Si(OEt)_2 + 2SF_4 \longrightarrow 3Me_2SiF_2 + 2(EtO)_2SO + 2EtF$$

It has been demonstrated that SF_4 reacts with trimethylphenoxosilane to yield $PhOSF_3$, $(PhO)_2SF_2$, $(PhO)_3SF$ and $(PhO)_4S$ and trimethylfluorosilane[116]. Oxyfluorides of S(IV) and S(VI) also react with alkoxosilanes[117].

$$SOF_2 + Me_3SiOMe \longrightarrow MeO\,S(O)F + (MeO)_2SO + Me_3SiF$$

$$SOF_4 + Me_3SiOMe \longrightarrow SO_2F_2 + MeF + Me_3SiF$$

However, SOF_2 does not react with Me_3SiOPh and SOF_4 yields the corresponding phenoxo derivatives of sulphur and Me_3SiF.

$$SOF_4 + Me_3SiOAr \longrightarrow ArOS(O)F_3 + Me_3SiF$$

(Ar = Ph, p-tolyl, p-ClPh, p-F Ph, p-NO_2Ph, C_6F_5)

Phosphorus pentafluoride and fluorophosphoranes react in similar fashion with Si-O compounds[118]. The reactions proceed with particular ease in the case of tetrafluorophosphoranes which react rapidly with evolution of heat, as does the parent compound PF_5, but Ph_2PF_3 is the only trifluorophosphorane to undergo this type of reaction and long heating periods are required. These reactions were originally investigated with a view to preparing pentacoordinate compounds of the

type RPF_3OR'' but like the corresponding SF_4 derivatives previously mentioned, the following type of reaction is observed.

$$RPF_4 + R_3'SiOR'' \longrightarrow RPOF_2 + R_3'SiF + R''F$$

It is suggested that the instability of the pentacoordinate phosphorus compounds and the formation of the tetracoordinate $RPOF_2$ is associated with the stability of the polar phosphoryl bond. Peake and Schmutzler[119] proposed that the above decomposition would be less pronounced with mercapto compounds, the P=S bond being less polar than the P=O bond and stable pentacoordinate fluorides of composition $R'_nPF_{4-n}SR''$ ($n = 1, 2$; $R' = Ph$; $R'' =$ alkyl, aryl) are obtained according to the equation;

$$R'_nPF_{5-n} + R''SSiMe_3 \longrightarrow R'_n PF_{4-n}SR'' + Me_3SiF$$

Stable fluorophosphoranes containing an aryloxo group are also obtained by a similar synthetic route with trimethylphenoxosilane but $RPF_2(OPh)_2$ ($R = Me, Ph$) rather than $RPF_3(OPh)$ is formed irrespective of the order of combination of reactants or their molar ratio[120].

The reaction of TeF_6 with silanols has been investigated[121]. Cleavage of the Si-O bond predominates rather than O-H bond cleavage,

$$TeF_6 + Me_3SiOH \longrightarrow TeF_5OH + Me_3SiF$$

in contrast to the reaction of TeF_6 with MeOH where O-H bond cleavage occurs producing TeF_5OMe and HF. TeF_5OMe[122] is isolated at 20°C as a colourless liquid. Alkoxotungsten[123] and molybdenum[124] fluorides can also be isolated at room temperature; for example.

$$WF_6 + Me_3SiOMe \longrightarrow WF_5OMe + Me_3SiF.$$

$$WF_5 + Me_2Si(OMe)_2 \longrightarrow WF_4(OMe)_2 + Me_2SiF_2$$

$$MoF_6 + Me_3SiOMe \longrightarrow MoF_5OMe + Me_3SiF$$

WF_5OMe decomposes slowly at 20°C to give WOF_4 and MeF.

The cleavage of silicon-element bonds by binary fluorides is not

limited to Si-O and Si-S bonds. Many examples of Si-N and Si-Cl cleavage have been reported. Equimolar quantitities of SF_4 and Me_3SiNR_2(R = Me, Et) react readily below room temperature to yield the corresponding SF_3NR_2 compounds[125]. The reaction of fluorophosphoranes, including PF_5, with Si-N compounds provides a simple route towards the synthesis of a variety of P-F-N compounds[118], which, in contrast to the P-F-O compounds previously described can, in general, be isolated at room temperature. Several dialkylamino derivatives of Te(VI)[126] and W(VI)[127] have also been prepared by reacting the hexafluoride with a Si-N compound. SF_4 converts Si-Cl bonds into Si-F groups, but SF_3Cl is not isolated. Instead, SCl_2 and Cl_2 are the other products[115]. PF_4Cl is prepared by the action of SbF_3 on PF_3Cl_2,[128] and TeF_5Cl is formed by the action of fluorine on $TeCl_4$. TeF_5Cl, so formed, is contaminated with free chlorine[129]. However, a comprehensive study of the formation of compounds WF_nCl_{6-n}(n = 0-6) in the reaction of WF_6 with excess Me_3SiCl demonstrated the ability of a weak fluorinating agent, WF_6, to form SiF bonds and that chlorofluoride derivatives of some elements can be prepared by cleaving Si-Cl bonds[130].

This method of preparing substituted derivatives of binary fluorides has the advantage that the fluorosilanes are volatile, generally easy to separate from the reaction mixture and show no evidence of complicating side reactions with other species in the mixture. The ease with which the reactions occur can, in part at least, be attributed to the high energy of the Si-F bond compared with bonds between silicon and other elements. Table 1 lists some silicon element bond energies for comparison[131].

/

TABLE 1

Bond	Average bond energies (K cal mol^{-1})	Compound
Si-F	135	SiF_4
Si-Cl	91	$SiCl_4$
Si-O	108	SiO_2(c)
Si-S	70	$(SiH_3)_2S$
Si-N	77	$(Me_3Si)_2NH$
Si-C	72	$Si(Me)_4$

The object of the present work was to extend these methods with a view to preparing substituted derivatives of iodine pentafluoride. Attempts to prepare methoxo derivatives of IF_5 by reacting $N(R)_4IF_6$ (R = Me, Et) with $As(OMe)_5$ in CH_3CN yielded I_2 as the only identifiable product[56]. $N(R)_4[IF_4(OC(O)CF_3)_2]$ is reported to be formed in the reaction of $N(R)_4IF_6$ with $(CF_3CO)_2O$ but is characterised only by its infrared spectrum. IF_4Cl[66] has been reported as an intermediate in the reaction

$$N(Et)_4Cl + IF_5 \rightarrow N(Et)_4IF_6 + N(Et)_4IF_4Cl_2$$

Attempts to repeat this work using CsCl and IF_5 led only to the formation of Cl_2 and $CsIF_6$[28].

Although the fluorination of organo-silicon compounds using IF_5 has not been extensively studied, its reactions with organic compounds have been investigated and are presented in a review[25]. The fluorination of phosphorous-oxygen bonds has been briefly described[32]. Phosphorus pentoxide and excess iodine pentafluoride, when slightly warmed, react to give phosphorus oxytrifluoride and iodine oxytrifluoride.

$$P_2O_5 + 3IF_5 \longrightarrow 2POF_3 + 3IOF_3$$

Phosphite esters react with other binary fluorides to

form P-F bonds. PF_5 and $P(OMe)_3$ form a 1:1 adduct which breaks down to give a mixture of P(V) and P(III) compounds containing P-O, P-C and P-F bonds. Similar compounds are formed by the action of SF_4[125] or WF_6[132] on phosphite esters.

The interaction of IF_5 with oxygen containing compounds of sulphur has also received some attention. Woolf[133] has demonstrated that IF_5 reacts with SO_3 giving a constant boiling mixture, $IF_5 \cdot 1.7SO_3$, which may contain $IF_4^+ SO_3F^-$, and with potassium persulphate IF_5 forms the complex $K_2S_2O_8 \cdot 1.02\ IF_5$. Lawless and Hennon[134] report that, although the reaction can be explosive, controlled fluorination of dimethyl sulphoxide by IF_5 produces $CH_2FS(O)H$ as a major product among many other compounds, in some of which the oxygen atom is transferred from sulphur to carbon, COS, CF_2O, HCFO etc. Other products include HF and small amounts of CF_4, CHF_3, CH_2F_2 and fluorinated sulphur compounds. However, in contrast to this work, Sharp and his co-workers[135], have shown that the major product from the reaction of SF_4 or WF_6 with D.M.S.O. has almost identical spectroscopic properties to the product formulated as $CH_2FS(O)H$ but is, in fact, CH_2FOCH_2F. Although the reaction with D.M.S.O. is complex, G. Haran[136] finds that IF_5 and $(CH_3O)_2SO$ react smoothly between -80^oC and -30^oC producing methylfluorosulphite as an identifiable product according to the equation:

$$IF_5 + (MeO)_2SO \longrightarrow IF_4OCH_3 + CH_3OS(O)F$$

In this case, IF_4OCH_3 was presumed to be the other product. Several other investigations have noted the formation of aryl and alkyl fluorosulphites. In particular, WF_6 and $(RO)_2SO$ (R=Me, Et, Ph) react with exchange of F and OR ligands producing $ROS(O)F$ and WF_5OMe, which is

isolated as a white crystalline solid[132]. On the other hand, SF_4 reacts with dimethyl sulphite to give $CH_3OS(O)F$, SOF_2 and CH_3F, the latter two products being derived from the intermediate SF_3OCH_3[137].

The substituted derivatives of IF_6^-, previously discussed, decompose readily so that they have not been characterised and the replacement of fluorine in IF_5 has not been studied in any detail. Prompted by the isolation of compounds such as WF_5OMe and TeF_5OMe and the proposed formation of IF_4OMe, this chapter describes a detailed investigation of substituted derivatives of IF_5 formed by exchange of fluorine with other ligands. To this end, reactions of IF_5 with organo silicon compounds containing mainly Si-OR, Si-Cl and Si-OC(O)R bonds have been studied. The reaction of IF_5 with $P(OMe)_3$ is investigated and the reaction of IF_5 with dialkyl sulphites is reinvestigated, both with a viewto preparing methoxo substituted derivatives of IF_5. The use of organosilicon compounds is extended to prepare higher substituted derivatives of IF_5 and derivatives of R_FIF_4 where the R_F group, in principle, may be used as a n.m.r. probe to follow the replacement of iodine fluorines by other ligands.

RESULTS and DISCUSSION

I The Reactions of Iodine Pentafluoride with Methylmethoxosilanes.

(a) Preparation and Properties of Alkoxo-iodine(V) Tetrafluorides.

IF_5 reacts with $Me_{4-n}Si(OR)_n$ (R = Me, Et; n = 1,2) exothermically at 20°C forming alkoxo-iodine(V) tetrafluorides, IF_4OR, and the corresponding methylfluorosilanes, according to the equations:

$$IF_5 + Me_3SiOMe \longrightarrow IF_4OMe + Me_3SiF \qquad 1.$$

$$2IF_5 + Me_2Si(OMe)_2 \longrightarrow 2IF_4OMe + Me_2SiF_2 \qquad 2.$$

$$IF_5 + Me_3SiOEt \longrightarrow IF_4OEt + Me_3SiF \qquad 3.$$

$$2IF_5 + Me_2Si(OEt) \longrightarrow 2IF_4OEt + Me_2SiF_2 \qquad 4.$$

Careful control of the reaction stoicheiometry is necessary to isolate IF_4OR pure. With a mole ratio of $Me_3SiOR:IF_5 > 1$ or $Me_2Si(OR)_2:IF_5 > 1:2$, more highly substituted derivatives are obtained. When $Me_3SiOR:IF_5 < 1$, Me_2SiF_2 and I_2 are also formed. Reactions between IF_5 and fluoromethylsilanes have been investigated and will be discussed later. Purer products are obtained when IF_5 and $Me_2Si(OR)_2$ are employed. Similar attempts to prepare IF_4OPh from IF_5 and Me_3SiOPh were unsuccessful as the phenoxo group is apparently fluorinated.

Methoxo-iodine(V) tetrafluoride is a volatile, white solid and ethoxo-iodine(V) tetrafluoride is a colourless liquid. Both compounds are moisture sensitive and decompose slowly at 20°C. IF_4OMe has been characterised by its analysis and mass spectrum (Table 2.1). The identities of $IF_4OCH_2^+$ and $IF_3OCH_3^+$ have been confirmed by mass measurement. The mass spectrum of IF_4OEt, displays a similar fragmentation pattern (Table 2:2.) Some features in the spectra are worthy of comment.

TABLE 2

Mass spectra of alkoxo-iodine(V) tetrafluorides.

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		I. IF_4OCH_3			
254	7	I_2^+	165	18	IF_2^+
234	1	$IF_4OCH_3^+$	146	9	IF^+
233	15	$IF_4OCH_2^+$	142	5	ICH_3^+
215	17	$IF_3OCH_3^+$	128	21	HI^+
203	21	IF_4^+	127	20	I^+
184	9	IF_3^+	31	100	OCH_3^+
181	28	IF_2O^+	29	76	OCH^+
		2. $IF_4OC_2H_5$			
254	46	I_2^+	162	2	IOF^+
247	2	$IF_4OC_2H_4^+$	156	5	$IC_2H_5^+$
234	1	$IF_4OCH_3^+$	155	1	$IC_2H_4^+$
233	25	$IF_4OCH_2^+$	146	5	IF^+
229	3	$IF_3OC_2H_5^+$	142	2	ICH_3^+
227	1	$IF_3OC_2H_3^+$	128	12	HI^+
209	4	$IF_2OC_2H_4^+$	127	26	I^+
203	38	IF_4^+	48	1	$FC_2H_5^+$
184	5	IF_3^+	47	2	$FC_2H_4^+$
181	9	IF_2O^+	45	54	$OC_2H_5^+$
172	3	$IOC_2H_5^+$	31	100	OCH_3^+
165	7	IF_2^+	30	13	OCH_2^+
163	2	$HIOF^+$	29	64	$C_2H_5^+$

No metastables were observed in the spectra, so the breakdown pattern is not clearly established but it appears that cleavage of the I-O bond is an important fragmentation pathway, as peaks assigned to IF_4^+ are abundant in both spectra. This may be contrasted with C-I bond cleavage in the spectra of R_FIF_4 where R_FI^+ rather than IF_4^+ is a major species in the spectrum. The peak corresponding to IOR^+ is not observed in the spectrum of IF_4OMe and is observed only as a relatively weak peak in the spectrum of IF_4OEt. The presence of ions, in the spectrum of IF_4OCH_3 in particular, corresponding to $IF_4OCH_2^+$ and $IF_3OCH_3^+$ suggests that loss of a proton and loss of a fluorine atom from the molecular ion are two possible fragmentation processes.

IF_4OMe is freely soluble in IF_5, C_6F_6 and CH_3CN without reaction. Table 3 lists the ^1H and ^{19}Fn.m.r. chemical shifts of IF_4OMe in these solvents and in benzene, with which it slowly reacts. The table also lists the chemical shifts of IF_4OEt. The ^{19}Fn.m.r. spectra of both compounds and the ^1H spectrum of IF_4OMe are single peaks. The ^1Hn.m.r. spectrum of IF_4OEt displays the expected ethyl signal, $J_{HH} = 7Hz$. The ^{19}F signal of IF_4OMe (half-height width at 33°C = 12Hz) sharpens on cooling and at -50°C a quartet, $J_{HF} = 2Hz$ is observed but no ^1H - ^{19}F coupling is observed in the spectrum of IF_4OEt, even at -60°C. However, the spectra are consistent with a square pyramidal structure in which the OR group occupies the apical position (Fig. 1) or with the presence of a fast exchange process. Therefore, it cannot be said with any certainty whether the molecules are monomeric or polymeric in solution, and because of the hygroscopic nature of these compounds

TABLE 3

^{1}H and ^{19}F spectra of IF_4OR.

Compound	Solvent	δ_F(p.p.m.)[a]	δ_H(p.p.m.)[b]	J_{HF}(Hz)	J_{HH}(Hz)
	CH_3CN[c]	9.0	4.33	2	
IF_4OMe	IF_5	5.1	4.61		
	C_6F_6	7.3	4.38		
	C_6H_6	1.4	3.60		
IF_4OEt	neat	6.0	4.73(CH_2) 1.40(CH_3)		7
	CH_3CN	3.9	4.90(CH_2) 1.43(CH_3)		7

a. Chemical shifts upfield from CCl_3F ext.

b. Chemical shifts downfield from TMS ext.

c. CCl_3F and T.M.S. internal reference.

Structure of IF_4OR

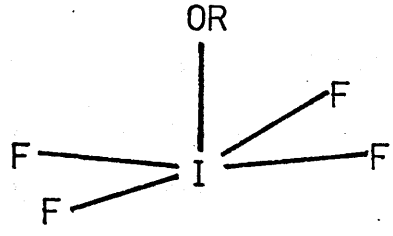


Fig. 1.

the molecular weight data obtained was not reproducible. Although no compound was isolated from the reaction of IF_5 and Me_3SiOPh, the ^{19}F n.m.r. spectrum of the mixture in acetonitrile contained a peak at δ = -4.7p.p.m., which may be due to IF_4OPh.

The infrared spectra of IF_4OMe and IF_4OEt comprise broad peaks around 560cm^{-1} consistent with I-F and I-O stretching frequencies. Strong bands at 962cm^{-1} in IF_4OMe and 984cm^{-1} in IF_4OEt are assigned to C-O stretches. Other bands in the spectra are consistent with the presence of alkyl groups. No structural information can be obtained from these spectra as the bands are broad, but a Raman spectrum may aid a determination of the symmetry of IF_4OR.

Reactions of IF_4OMe

The reactions of IF_4OMe with some organosilicon compounds and $P(OMe)_3$ will be discussed later.

IF_4OMe forms a 1:1 adduct with pyridine. The i.r. and n.m.r. spectra are consistent with the formation of a methyl pyridinium salt. In particular, bands in the i.r. spectra at 776 and 679cm^{-1} correspond to bands at 764 and 675cm^{-1} in the spectrum of $C_5H_5NMe^+$ TeF_5O^- which is formed from pyridine and TeF_5OMe[138]. By comparison, the adduct of IF_4OMe with pyridine may be tentatively formulated as $C_5H_5NMe^+$. IF_4O^-, although no evidence for the anion has been obtained. However, the structure of Cs^+ IOF_4^- has recently been determined.[173].

A mixture of IF_4OMe and trimethylamine explodes below 20°C. However, more careful control of the reaction conditions may lead to the isolation of the tetramethyl-ammonium salt, $\dot{N}(CH_3)_4.IOF_4^-$.

It was thought that IF_4OMe might also methylate benzene according to:

$$C_6H_6 + IF_4OMe \longrightarrow C_6H_5Me + IOF_3 + HF \qquad 5.$$

There is evidence that WF_5OMe and benzene react slowly to form toluene[139]. Although several new CH_3 resonances appear in the ^{1}Hn.m.r. spectrum of the product after three days, none can obviously be assigned to the methyl group of toluene. However, a slow reaction does occur at 20°C in which HF is produced. There is considerable evidence to suggest that ring fluorination occurs. A low intensity peak in the ^{19}Fn.m.r. spectrum at δ -143 p.p.m. is consistent with the presence of fluorine in the benzene ring. Also, fragments in the mass spectrum at $^{m}/_{e}$ = 115 and 96 are assigned to the ions $C_6H_4F_2^+$ and $C_6H_5F^+$ respectively. A doublet at δ + 18p.p.m. and a singlet at δ-173p.p.m. are tentatively assigned to IF_5 and IF_3 or a derivative of IF_3. The fluorination of the ring may therefore occur with reduction of IF_4OMe to an I(III) compound, IF_5 resulting from disproportionation of the I(III) species. The spectra of the products from the reaction between IF_5 and Me_3SiOPh also indicate fluorination of the phenoxo group. In contrast to the products postulated above, the reaction of IF_5 and benzene proceeds smoothly at room temperature to form iodobenzene, HF and tar, together with unreacted IF_5. Di- and tri-iodobenzene are also produced in small yields but fluorobenzene and fluoroiodobenzene are not detected[25].

IF_4OMe reacts with AsF_5 below room temperature. The infrared spectrum of the initial liquid product contains bands at 920cm^{-1}, C-O stretch, 600cm^{-1}, I-F and I-O stretches, and a band at 710cm^{-1} assigned to an As-F stretch. This product contains one methyl resonance in its ^{1}Hn.m.r. spectrum and one major signal in the ^{19}Fn.m.r. spectrum, which may have satellite peaks , J ~ 320Hz.

This signal may be an average of the I-F and As-F chemical shifts caused by fluorine exchange. The liquid product decomposes in CCl_3F giving an unidentified volatile product which contains Me and F from its ^{19}Fn.m.r. spectrum, and a crystalline solid. The infrared spectrum of this product contains a peak at $705cm^{-1}$ consistent with an AsF_6^- group. It may that the initial product is a complex between IF_4OMe and AsF_5 which decomposes *via* a fluoride transfer mechanism to give an adduct, which may be similar to that formed in the reaction between CF_3IF_4 and AsF_5, where I(V) is apparently reduced to I(III).

Decomposition of IF_4OR

The thermal stabilities of IF_4OR are in the order Me>Et. They are intermediate between the methoxofluorides of non-metals like PF_4OMe, which has been identified by n.m.r. spectroscopy only at low temperature[140], and TeF_5OMe[122]. The decomposition of several alkoxofluorides has been postulated to occur *via* formation of an alkyl cation:

$$R \text{—} O \text{—} XF_n \text{—} F \longrightarrow O = XF_n + R^+ + F^-$$

When X = S, P or W the corresponding alkyl fluoride is formed. However, the decomposition of IF_4OMe observed over ten days at 20°C does not produce MeF, but SiF_4 is observed suggesting HF is formed in the decomposition. The other volatile product contains a C=O group, from its infrared spectrum, and is thought to be formaldehyde. The other products are iodine and an unidentified white solid which may contain a terminal I=O bond, from its infrared spectrum.

As HF attacks glass, producing H_2O, a complete decomposition scheme will be complicated but initial formation of HF and CH_2O can be rationalised as follows:

$$IF_4OCH_3 \longrightarrow IF_3 + CH_3OF$$

$$IF_5 + I_2 \qquad CH_2O + HF$$

A molecule of the type CH_3OF would be expected to decompose as shown. IF_5 is not detected but as it is readily hydrolysed by water it may form oxyfluorides. The decomposition process need not be intramolecular.

The scheme above is similar to the decomposition route proposed for CF_3IF_4, where fluorine transfer from iodine to carbon is invoked. In this instance, fluorine would be transferred from iodine to oxygen. However, the I-F bond energy in IF_5 is 64K cal mol^{-1} and the O-F bond energy in OF_2 is 51 k cal mol^{-1} [78]. Therefore, on bond energy data, formation of CH_3OF is not a thermodynamically favourable process, but the subsequent formation of CH_2O and HF from CH_3OF is favourable due to the relatively strong H-F&C=O bonds. It may be related that alkoxides of boron, aluminium, gallium and silicon decompose in the mass spectrometer with elimination of neutral carbonyl species[141].

The decomposition of IF_4OEt, by analogy, should produce CH_3CHO and HF. The products of the decomposition of IF_4OEt were not investigated but decomposition of the products of a reaction designed to produce $IF_3(OEt)_2$ indicate the presence of CH_3CHO.

(b) Preparation of Higher Substituted Alkoxo-derivatives of Iodine Pentafluoride.

Polysubstituted alkoxo-derivatives of IF_5 are prepared by reacting IF_5 or IF_4OR with methylalkoxosilanes at 20°C according to the following equations:

$$IF_5 + 2Me_3SiOMe \longrightarrow IF_3(OMe)_2 + 2Me_3SiF \quad 6.$$

$$IF_5 + Me_2Si(OMe)_2 \longrightarrow IF_3(OMe)_2 + Me_2SiF_2 \quad 7.$$

$$IF_4OMe + Me_3SiOMe \longrightarrow IF_3(OMe)_2 + Me_3SiF \quad 8.$$

$$IF_5 + Me_2Si(OEt)_2 \longrightarrow IF_3(OEt)_2 + Me_2SiF_2 \quad 9.$$

$$IF_4OMe + Me_3SiOEt \longrightarrow IF_3(OMe)(OEt) + Me_3SiF \quad 10.$$

$$2IF_5 + 3Me_2Si(OMe)_2 \longrightarrow 2IF_2(OMe)_3 + 3Me_2SiF_2 \quad 11.$$

$$IF_5 + 2Me_2Si(OMe)_2 \longrightarrow IF(OMe)_4 + 2Me_2SiF_2 \quad 12.$$

$$IF_5 + 5Me_3SiOMe \longrightarrow I(OMe)_5 + 5Me_3SiF \quad 13.$$

$$2IF_5 + 5Me_2Si(OMe)_2 \rightarrow 2I(OMe)_5 + 5Me_2SiF_2 \quad 14.$$

The reactions are summarised in the experimental section (Table11). Reactions 6-8 produce colourless or pale pink liquids which move slowly in vacuo and analyse as $IF_3(OCH_3)_2$. The ^{19}Fn.m.r. i.r. and mass spectrometric data on the three products are reproducible but the ^{19}Fn.m.r. and mass spectra are not easily assigned in terms of a pure compound. The spectra of the other disubstituted products are also complicated. $IF_2(OMe)_3$ is a colourless liquid characterised by analysis. $IF(OMe)_4$ and $I(OMe)_5$ are also colourless liquids, involatile at room temperature. They were not isolated pure. $I(OMe)_5$ was contaminated with trace amounts of $IF(OMe)_4$. These liquids decompose at room temperature. $IF_3(OMe)_2$ decomposes at 20°C over several days to give CH_2O, Me_2O, HF and I_2 among the products. At 100°C a mixture of $IF_3(OMe)_2$ and $IF_2(OMe)_3$ decomposes quickly producing CO and HI, in addition to the above products. $I(OMe)_5$ decomposes overnight to give I_2, CH_2O, Me_2O and another unidentified product which appears to contain carbon, hydrogen and oxygen.

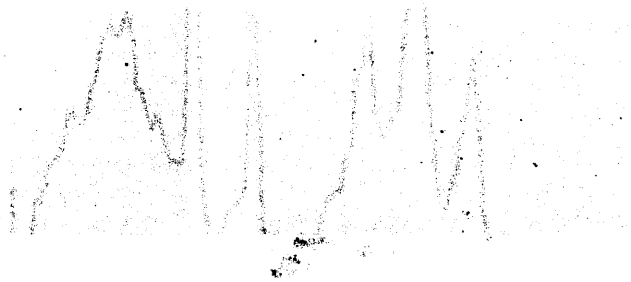
The ^{19}F and ^{1}H chemical shifts are listed in Table 4. The ^{19}F spectra of the disubstituted compounds contain more peaks than can be accounted for in terms of a pure compound. The higher substituted derivatives give rise to single peaks which occur to higher fields of IF_5 with increasing substitution of F by OR. A similar trend is found in the ^{1}H chemical shifts, although it is not as marked. As no $^{19}F - ^{19}F$ or $^{19}F - ^{1}H$ couplings are detected in the spectra, even at low temperatures, they cannot be unambiguously assigned. The ^{1}Hn.m.r. spectra of the compounds $IF_{5-n}(OMe)_n$ show a single methyl resonance. If $I(OMe)_5$ has a square pyramidal

TABLE 4

Chemical shifts of $IF_{5-n}(OR)_n$ (p.p.m.)

Compound	solvent	$-\delta_F$	δ_H
IF_4OMe	CD_3CN	9.0	4.33
$IF_3(OMe)_2$	CD_3CN	5.6 8.4 14.2	4.19
$IF_2(OMe)_3$	neat liquid	11.6	4.04
$IF(OMe)_4$	CD_3CN	20.3	3.80
$I(OMe)_5$	CH_3CN		3.86
IF_4OEt	CH_3CN	6.0	4.90(CH_2) 1.43(CH_3)
$IF_3(OEt)_2$ [a]	Me_2SiF_2	13.0(width at half-ht= 200Hz)	5.00(CH_2) 1.21(CH_3)
$IF_3(OMe)(OEt)$ [a]	CH_3CN	3.2 6.2 8.7 12.9 14.9 16.9	4.52 (CH_2) 1.34 (CH_3) } OEt 4.12 OMe

a external CCl_3F and TMS references



^{19}F N.M.R. SPECTRA of $IF_3(OMe)_2$ & $IF_3(OMe)(OEt)$

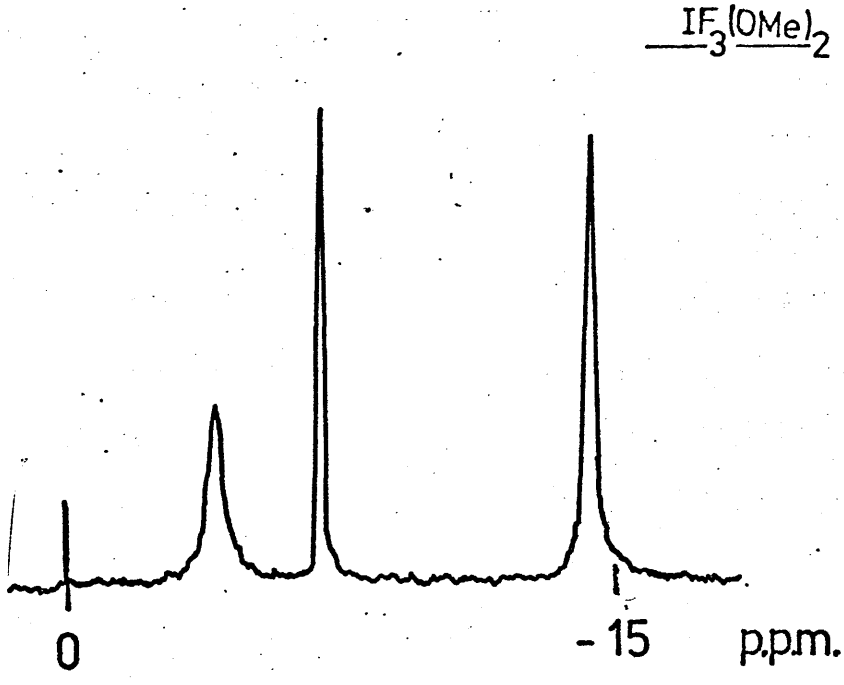


Fig.2a.

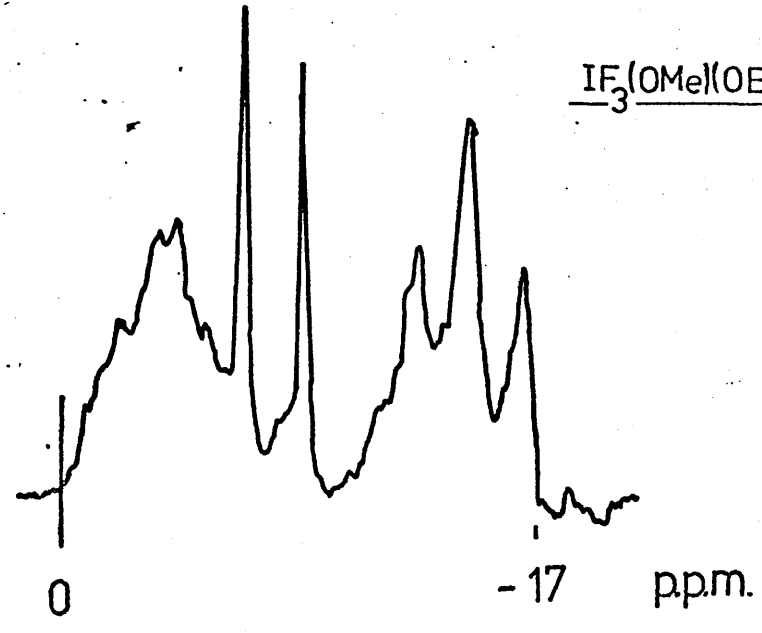


Fig.2b.

structure similar to IF_5, two methyl signals, an axial and an equatorial, are predicted. The presence of one peak suggests that either a fast inter or intramolecular exchange process is occurring, or the chemical shifts of the axial and equatorial OMe groups are not significantly different. An exchange process is thought more likely.

The ^{19}Fn.m.r. spectrum of the disubstituted compound $IF_3(OMe)_2$ contains peaks at δ-5.6 (width at half-ht = 60Hz), -8.4 (width at half-ht ~ 20Hz), -14.2p.p.m. (width at half-ht. = 30Hz), in the approximate intensity ratio of 1:1:2 (Fig.2a). By comparison with the low temperature spectrum of $CF_3IF_3(OMe)$ (Section II), the signals at δ-5.6 and -14.2p.p.m. may be assigned to $IF_3(OMe)_2$ and the signal at δ-8.4p.p.m. to IF_4OMe. IF_4OMe could arise from the following redistribution reaction.

$$2IF_3(OMe)_2 \longrightarrow IF_4OMe + IF_2(OMe)_3 \qquad 15.$$

In this case $IF_2(OMe)_3$ is not observed. On the same basis, the signals in the ^{19}Fn.m.r. spectrum of $IF_3(OMe)(OEt)$ at δ-6.2 and -8.7p.p.m. (Fig. 2b) can be assigned to IF_4OEt and IF_4OMe respectively. The other signals cannot be readily assigned, but the three high field signals may be a triplet, J= 124Hz, and a ^{19}F - ^{19}F decoupling might aid assignment of these spectra. Another explanation of these signals is that they may be due to fluorine in chemically different environments in some sort of polymeric chain, with the broad resonances due to bridging fluorines.

The ^{19}Fn.m.r. spectrum of $IF_2(OMe)_3$ can be rationalised in terms of a structure with two equivalent fluorines; for example (a & b)

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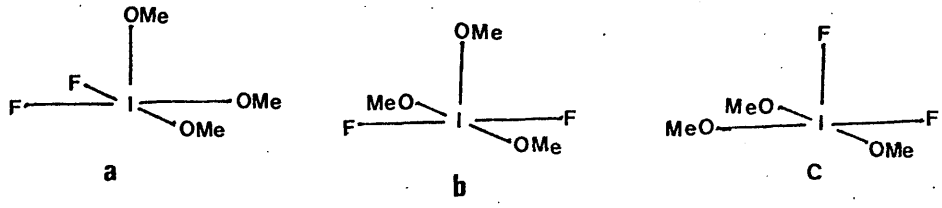


Fig. 3.

or with a fast exchange process in c

The ^{19}Fn.m.r. spectra of these compounds are not very useful. Hence, substitution at CF_3IF_4 was investigated to throw more light on the problem.

The infrared spectra of $IF_{5-n}(OMe)_n$ are similar to those already described for IF_4OMe. It may be significant that, in the spectra of $IF_{4-n}(OMe)_n$, the centre of the broad band at 560-500cm^{-1} moves to lower energy as n increases. The I-O stretch is expected to occur at lower energy than the I-F stretch. The band at 962cm^{-1} in the spectrum of IF_4OMe, assigned to a C-O stretch moves to higher energy as the degree of substitution increases.

These alkoxoiodine(V) fluorides are best characterised by their mass spectra (Table 5). The mass spectra of $IF_3(OMe)_2$ and $IF_3(OMe)(OEt)$ contain peaks attributable to the molecular ion, M^+, and $(M-H)^+$, and the spectrum of $IF_3(OEt)_2$ shows a characteristic ion at $^m/_e$ 273, assigned to $(M-H)^+$. The mass spectrum of $IF_2(OMe)_3$ does not contain a molecular ion, but $^m/_e$ =257 is readily assigned to $(M-H)^+$. In the spectra of $IF(OMe)_4$ and $I(OMe)_5$ peaks at $^m/_e$ = 251 and 239 are assigned to $I(OMe)^+_4$ and $IF(OMe)^+_3$ respectively.

The mass spectra of the disubstituted products contain peaks consistent with corresponding monosubstituted products. In the spectrum of $IF_3(OMe)_2$, $^m/_e$ = 233 and 203 are assigned to $IF_4OCH_2^+$

TABLE 5

Mass Spectra of $IF_{5-n}(OR)_n$ (n 2-5)

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		1. $IF_3(OMe)_2$			
254	29	I_2^+	177	4	$IFOCH_3^+$
246	< 0.5	$IF_3O_2C_2H_6^+$	165	19	IF_2^+
245	< 0.5	$IF_3O_2C_2H_5^+$	163	5	$HIFO^+$
233	4	$IF_4OCH_2^+$	162	7	IFO^+
227	4	$IF_2O_2C_2H_6$	158	6	$IOCH_3^+$
215	17	$IF_3OCH_3^+$	157	3	$IOCH_2^+$
211	4	$IF_2O_2CH_2^+$	146	7	IF^+
203	7	IF_4^+	142	4	ICH_3^+
196	2	$IF_2OCH_3^+$	128	9	HI^+
195	3	$IF_2OCH_2^+$	127	20	I^+
193	3	$IFO_2CH_3^+$	31	100	OCH_3^+
184	3	IF_3^+	29	76	OCH^+
181	18	IF_2O^+			

Metastable Transitions

m_1	Transition	m_2	m^* obsd.	m^* cald.
215	$IF_3OCH_3^+ \longrightarrow IF_2O^+ + MeF^{\cdot}$	181	152.4	152.3
246	$IF_3(OCH_3)_2^+ \longrightarrow IF_3^+ + MeOOMe^{\cdot}$	184	~138	137.6
227	$IF_2(OCH_3)_2^+ \longrightarrow IFOMe^+ + MeOF^{\cdot}$	177		138.0
162	$IFO^+ \longrightarrow I^+ + OF^{\cdot}$	127	99.8	99.6
181	$IF_2O^+ \longrightarrow I^+ + OF_2^{\cdot}$	127	88.8	89.1
227	$IF_2(OCH_3)_2^+ \longrightarrow CH_3I^+ + CH_3O_2F_2^{\cdot}$	142		88.8

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		2. $IF_2(OMe)_3$			
257	0.2	$IF_2O_3C_3H_8^+$	177	4	$IFOCH_3^+$
254	39	IF_2^+	165	6	IF_2^+
245	0.2	$IF_3O_2C_2H_5^+$	163	1	$HIFO^+$
239	0.2	$IFO_3C_3H_9^+$	162	0.2	IFO^+
233	1	$IF_4OCH_2^+$	158	4	$IOCH_3^+$
227	4	$IF_2O_2C_2H_6^+$	157	2	$IOCH_2^+$
215	14	$IF_3OCH_3^+$	146	4	IF^+
211	0.2	$IF_2O_2CH_2^+$	142	6	ICH_3^+
203	2	IF_4^+	128	8	HI^+
196	0.2	$IF_2OCH_3^+$	127	25	I^+
195	1	$IF_2OCH_2^+$	31	100	OCH_3^+
193	1	$IFO_2CH_3^+$	29	100	OCH^+
184	1	IF_3^+			
181	9	IF_2O^+			

Metastable Transitions

m_1	Transition	m_2	m^* obsd.	m^* calcd.
215	$IF_3OCH_3^+ \longrightarrow IF_2O^+ + MeF^{\cdot}$	181	152.3	152.3
246	$IF_3(OCH_3)_2^+ \longrightarrow IF_3^+ + MeOOMe^{\cdot}$	184	~138	137.6
227	$IF_2(OCH_3)_2^+ \longrightarrow IFOCH_3^+ + MeOF^{\cdot}$	177		138.0

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		3. $IF(OMe)_4$			
254	24	I_2^+	163	1	$HIFO^+$
251	0.5	$I(OCH_3)^+$	162	0.3	IFO^+
239	3	$IF(OCH_3)_3^+$	158	3	$IOCH_3^+$
227	4	$IF_3OCH_3^+$	157	2	$IOCH_2^+$
215	0.4	$IF_3OCH_3^+$	146	1	IF^+
208	< 0.5	IFO_2CH_6	143	1	IO^+
195	0.5	$IF_2OCH_2^+$	142	4	ICH_3^+
193	2	$IFO_2CH_3^+$	128	2	HI^+
189	1	$IO_2C_2H_6^+$	127	12	I^+
181	0.3	IF_2O^+.	31	83	OCH_3^+
177	5	$IFOCH_3^+$	30	37	OCH_2^+
165	1	IF_2^+	29	100	OCH^+

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		4. $I(OMe)_5$			
254	60	I_2^+	163	5	$HIFO^+$
251	0.3	$I(OCH)_4^+$	162	1	IFO^+
239	11	$IFO_3C_3H_9^+$	158	13	$IOCH_3^+$
227	55	$IF_2O_2C_2H_6^+$	157	5	$IOCH_2^+$
215	4	$IF_3OCH_3^+$	146	1	IF^+
208	1	$IFO_2C_2H_6^+$	144	1	HIO^+
196	3	$IF_2OCH_3^+$	143	2	IO^+
195	4	$IF_2OCH_2^+$	142	7	ICH_3^+
193	11	IF_2OC^+ / $IFO_2CH_3^+$	128	4	HI^+
189	1	$IO_2C_2H_6^+$	127	23	I^+
181	2	IF_2O^+	31	100	OCH_3^+
177	22	$IFOCH_3^+$	30	52	OCH_2^+
165	7	IF_2^+	29	100	OCH^+

Metastable Transitions

m_1	Transition	m_2	m^* obsd.	m^* calcd.
246	$IF_3O_2C_2H_6^+ \longrightarrow IF_3^+ + C_3H_6O_2^\cdot$	184	~138	137.6
227	$IF_2O_2C_2H_6^+ \longrightarrow IFOCH_3^+ + CH_3OF^\cdot$	177		138.0
239	$IFO_3C_3H_9^+ \longrightarrow IFOCH_3^+ + C_3H_6O_2^\cdot$	177		131.1
163	$HIFO^+ \longrightarrow IF^+ + OH^\cdot$	146	~131	130.7
158	$IOCH_3^+ \longrightarrow HIO^+ + CH_2^\cdot$	144		131.2

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		5. $IF_3(OEt)_2$			
273	0.1	$IF_3OC_2H_5OC_2H_4^+$	181	4	IF_2O^+
259	1	$IF_3O_2C_3H_7^+$	179	0.5	$HIFO_2^+$
255	0.3	$IF_2O_2C_4H_{10}^+$	177	0.1	$IFOCH_3^+$
254	48	I_2^+	172	0.5	$IOC_2H_5^+$
247	0.3	$IF_4OC_2H_4^+$	165	3	IF_2^+
246	0.1	$IF_4OC_2H_3^+$	163	1	$HIFO^+$
233	4	$IF_4OCH_2^+$	162	1	IFO^+
229	6	$IF_3OC_2H_5^+$	157	0.2	$IOCH_2^+$
222	0.4	$IF_3OC_2H_3^+$	156	0.3	$IC_2H_5^+$
211	2	$IF_2O_2CH_2^+$	146	5	IF^+
210	0.1	$IF_2OC_2H_5^+$ $IF_2O_2CH^+$	144	0.3	HIO^+
209	2	$IF_2OC_2H_4^+$	143	0.2	IO^+
207	0.3	$IF_2OC_2H_2^+$	142	10	ICH_3^+
203	5	IF_4^+	141	6	ICH_2^+
201	1	HIF_3O^+	128	2	HI^+
199	0.6	$IF_3CH_3^+$	127	40	I^+
195	0.4	$IF_2OCH_2^+$	45	100	$OC_2H_5^+$
191	0.2	$IFOC_2H_5^+$	31	>100	OCH_3^+
184	0.1	IF_3^+	30	20	OCH_2^+
			29	>100	$C_2H_5^+$ OCH^+

Metastable Transitions

m_1	Transition	m_2	m^* obsd.	m^* calcd.
259	$IF_3O_2C_3H_7^+ \longrightarrow IF_3OC_2H_5^+ + OCH_2^\cdot$	229	202.5	202.8

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		6. $IF_3(OMe)(OEt)$			
260	0.3	$IF_3OCH_3OC_2H_5^+$	181	21	IF_2O^+
259	3	$IF_3O_2C_3H_7^+$	179	3	$HIFO_2^+$
254	27	I_2^+	177	3	$IFOCH_3^+$
245	5	$IF_4OC_2H_4^+$	172	4	$IOC_2H_5^+$
241	2	$IF_2\ O_2C_3H_8^+$	165	15	IF_2^+
233	10	$IF_4OCH_2^+$	163	6	$HIFO^+$
229	8	$IF_3OC_2H_5^+$	162	5	IFO^+
227	4	$IF_3OC_2H_3^+$	158	4	$IOCH_3^+$
215	22	$IF_3OCH_3^+$	157	3	$IOCH_2^+$
213	3	$IF_2OC_2H_4^+$	156	2	$IC_2H_5^+$
211	3	$IF_2O_2C_2H_2^+$	146	9	IF^+
209	6	$IF_2OC_2H_4^+$	144	2	HIO^+
207	1	$IF_2O_2CH_2^+$	143	2	IO^+
203	18	IF_4^+	142	6	ICH_3^+
201	5	HIF_3O^+	141	1	ICH_2^+
199	2	$IF_3CH_3^+$	128	5	HI^+
196	2	$IF_2OCH_3^+$	127	23	I^+
195	3	$IF_2OCH_2^+$	47	11	$FC_2H_4^+$
193	5	$IFO_2CH_3^+$ / IF_2OC^+	46	8	$FC_2H_3^+$
191	1	$IFOC_2H_5^+$	45	21	$OC_2H_5^+$
185	1	HI^+	31	70	OCH_3^+
184	5	IF_3^+	30	29	OCH_2^+
			29	100	$C_2H_5^+$ / OCH^+

Metastable Transitions

m_1	Transition	m_2	m^* obsd.	m^* calcd.
245	$IF_3OC_2H_5^+ \longrightarrow IF_3OCH_3^+ + CH_2^{\cdot}$	215	188.5–189.2	188.7
227	$IF_3OC_2H_3^+ \longrightarrow IF_2OC_2H_2^+ + HF^{\cdot}$	203		188.8

contd./

Metastable Transitions

m_1	Transition	m_2	m^* osbd.	m^* cald.
213	$IF_2O_2C_2H_4^+ \rightarrow IFOC_2H_3^+ + HF^{\cdot}$	193	174·4	174·4
215	$IF_3OCH_3^+ \longrightarrow IF_2^+ + CH_3OF^{\cdot}$	165	~127	126.6
177	$IFOCH_3^+ \longrightarrow IF^+ + OCH_3^{\cdot}$	146	120.4	120.4
196	$IF_2OCH_3^+ \rightarrow IF^+ + CH_3OF^{\cdot}$	146	109.0	108.8

and IF_4^+, and the spectrum of $IF_3(OMe)(OEt)$ contains ions at m/e = 247, 233 and 203 which can also be assigned to the tetrafluoro species $IF_4OC_2H_5^+$, $IF_4OCH_2^+$ and IF_4^+. Similar ions are observed in the spectrum of $IF_3(OEt)_2$. This supports the n.m.r. spectral assignments made for these disubstituted compounds, in that they contain substantial amounts of the monosubstituted derivative.

However, the spectra of $IF_2(OMe)_3$ and $IF(OMe)_4$ also contain ions which are assigned to species containing more fluorines than the molecular ion. For example, in the spectrum of $IF_2(OMe)_3$, the ions $IF_4OCH_2^+$, $IF_3OCH_3^+$, IF_4^+ and IF_3^+ are observed, and in the spectrum of $IF(OMe)_4$, $IF_2(OMe)_2^+$, $IF_3(OMe)^+$, $IF_2OCH_2^+$, IOF_2^+ and IF_2^+ are observed, which is inconsistent with their ^{19}Fn.m.r. spectra. This implies that the higher fluorinated species may be formed in the mass spectrometer. If the alkoxo-iodine fluorides are monomeric, the formation of these ions requires ion-molecule reactions. These occur in the ionization chamber of the mass spectrometer, where the percentage of molecules ionized in the vapour is very low. Consequently, the probability of a collision between an ion and a neutral molecule, during which an atom or group may be abstracted from the neutral molecule is finite. The abundance of the ions so formed depends upon the square of the sample pressure as they are formed by a second order process, and at the low sample pressures used in routine work, these ions are normally of negligible abundance. Such processes usually result in the formation of ions heavier than molecular ion[142]. In the present work, no ions heavier than the molecular ion, which are attributable to alkoxo-iodine fluorides, are observed. If these alkoxo fluorides are polymeric with fluorine bridges, a mechanism can be visualised, whereby fluorine is transferred from one iodine to another in the

mass spectrometer, with subsequent displacement of an OMe group. The first step may be loss of an OMe group, then transfer of fluorine, for no ions are observed with more OMe groups than the molecular ion. In support of this argument it may be significant that OCH_3^+ occurs in large abundance in the spectra. However, the formation of the ion OCH_3^+, $^m/_e = 31$, is also a favourable process in the mass spectra of alcohols, methyl ethers and methyl esters. The ion formed from methyl esters has the structure $CH_3{-}O^+$ with $\Delta H_f = 202$ K cal mol^{-1} [143], whereas the ion formed in the spectra of alcohols and methyl ethers[144] is formulated as $CH_2{=}OH^+$, $\Delta H_f = 174$ K cal mol^{-1}.

The spectra of the polysubstituted derivatives, unlike those of the monosubstituted derivatives previously discussed, contain metastable peaks. Several of the peaks observed are diffuse and of low intensity and more than one transition can be assigned to these metastables. For example the peak at $^m/_e = 138$ is observed in some of the spectra and two transitions are possible.

$$IF_3(OCH_3)_2^+ \longrightarrow IF_3^+ + CH_3OOCH_3$$

$$IF_2(OCH_3)_2^+ \longrightarrow IFOCH_3^+ + CH_3OF$$

These transitions are similar to the decomposition processes of these compounds, where elimination of an organic fragment accompanies reduction of the iodine. The metastable observed at $^m/_e = 152.4$ and assigned to the transition

$$IF_3OCH_3^+ \longrightarrow IF_2O^+ + CH_3F$$

is of interest in that an alkyl fluoride is formed. This can be compared with the decomposition pathways proposed for the alkoxyfluorides of tungsten, phosphorus and sulphur, in which a double bond is formed to the central atom. Presumably the above

disproportionation takes place via a four centre transition state:-

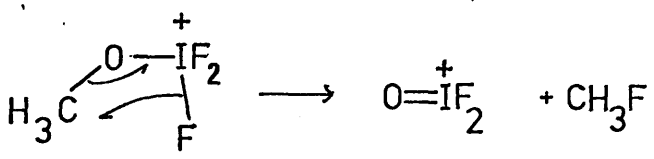


Fig. 4.

That a similar rearrangement does not take place outwith the mass spectrometer may indicate alkoxo-iodine(V) fluorides are polymeric, and elimination of F^- or formation of I=O double bonds is not a favourable process.

II Preparation of Methoxoderivatives of R_FIF_4.

R_FIF_4 (R_F = CF_3, C_2F_5, $(CF_3)_2CF$, C_4F_9, C_6F_5) react with trimethylmethoxo- or dimethylmethoxo-silane in CCl_3F at 20°C, with the replacement of I-F by I-OMe groups and the formation of Me_3SiF or Me_2SiF_2. The rate or degree of substitution of F by OMe at 20°C does not appear to depend on the R_F group. As the derivatives $CF_3IF_{4-n}(OMe)_n$ gave simpler ^{19}Fn.m.r., infrared and mass spectra, they were investigated more thoroughly and will be discussed in detail.

Reactions designed to produce individual members of the series $CF_3IF_{4-n}(OMe)_n$ give colourless liquids, which decrease in volatility as n increases. $CF_3I(OMe)_4$ is involatile. Decomposition is apparent within 0.5h at 20°C but total decomposition takes several hours. The decomposition products include HF, CH_2O, CF_4, CF_3I, and I_2. When $n > 2$, no CF_4 is observed and Me_2O is a possible product . The compounds $CF_3IF_{4-n}(OMe)_n$ are stable in solution for longer periods, and the species present are identified by their n.m.r. spectra (Table 6.) Their mass spectra (Table 8.)

TABLE 6

N.m.r. spectra of involatile liquids from reactions of CF_3IF_4 with methyl(methoxo) silanes

No.	Reactants (m.mol.)[a] CF_3IF_4	OMe	Compounds identified	^{19}F Spin System[b]	Chemical Shifts(p.p.m.)[c] $\delta(^{19}F)$	$\delta(^1H)$	Coupling Constants(Hz)
1	3.0	3.1	CF_3IF_4	A_3X_4	-33.4(F_X)		$^3J_{AX}$ = 18
					-57.6(F_A)		
			$CF_3IF_3(OMe)$	A_3M_2X	-7.0 (F_X)	3.91	$^3J_{AM}$ = 17
					-46.5 (F_M)		$^3J_{AX}$ = 25
					-56.6(F_A)		$^2J_{MX}$ = 113
			$CF_3IF_2(OMe)_2$	A_3X_2	-23.3(F_X)		$^3J_{AX}$= 24
					-59.1 (F_A)		
2	1.7	3.4	$CF_3IF_2(OMe)_2$	A_3X_2	-21.9 (F_X)	4.34	$^3J_{AX}$ = 24
					-58.3 (F_A)		
3	1.8	5.4	$CF_3IF_2(OMe)_2$[d]	A_3X_2	-21.0(F_X)		$^3J_{AX}$ = 23
					-58.2(F_A)	4.20	
			$CF_3IF(OMe)_3$	A_3X	-33.3(F_X)		$^3J_{AX}$ = 22
					-56.8(F_A)		$^3J_{AX}$ = 22
			$CF_3I(OMe)_4$	A_3	-55.4		
4	1.25	5.0	$CF_3IF(OMe)_3$	A_3X	-35.7(F_X)		$^3J_{AX}$ = 22

No.	Reactants (m.mol.) CF_3IF_4	OMe	Compounds identified	^{19}F Spin System	Chemical Shifts (p.p.m.)[c]		Coupling Constants(Hz)
					-57.5(F_A)	4.15	
4			$CF_3I(OMe)_4$	A_3	-55.8		

a. Me_3SiOMe $Me_2Si(OMe)_2$ x 2 b. neglecting ^1H - ^{19}F coupling c F CCl_3F internal or Me_4Si external

^{19}F N.M.R. SPECTRUM of $CF_3IF_{4-n}(OMe)_n$ from Reaction 1

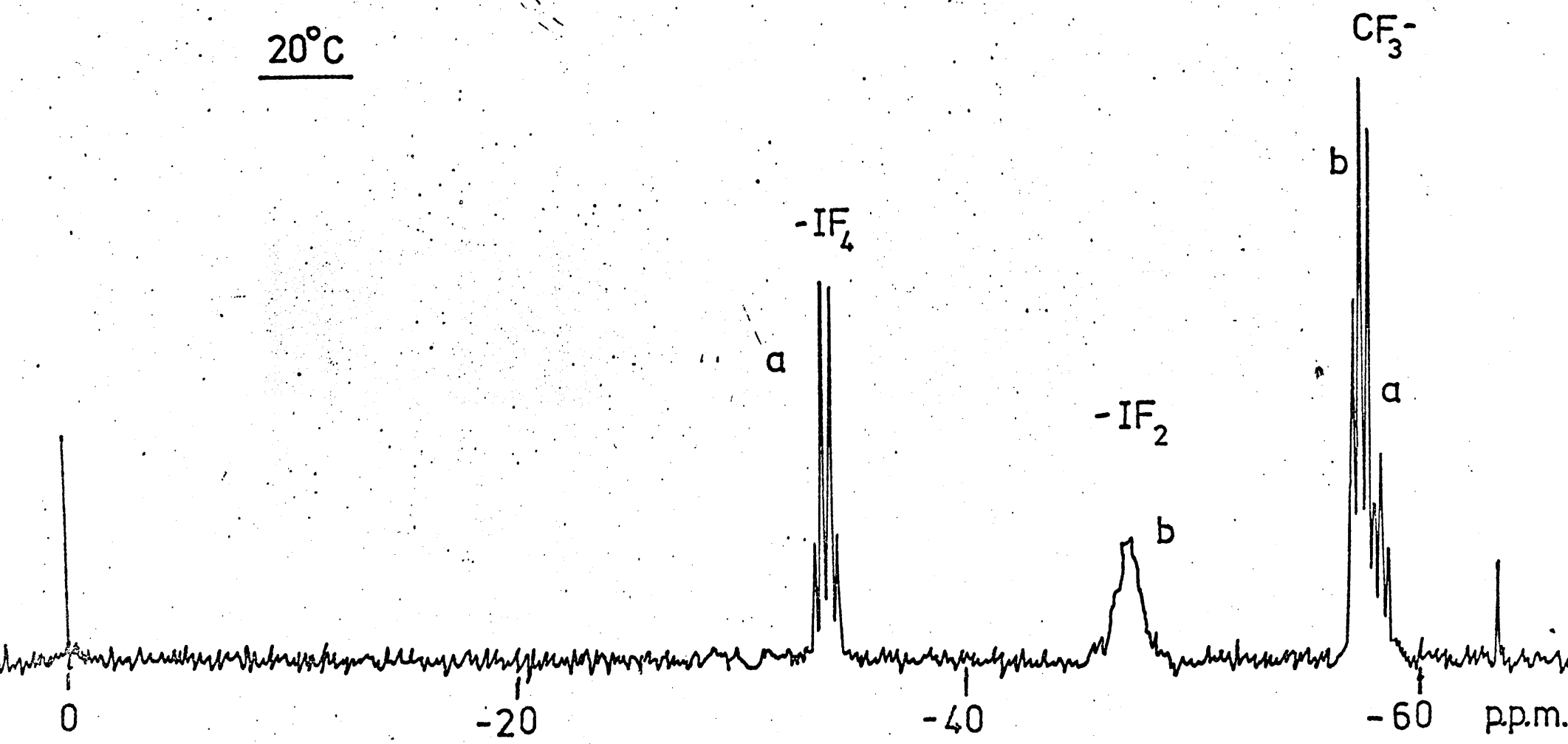


Fig.5.a

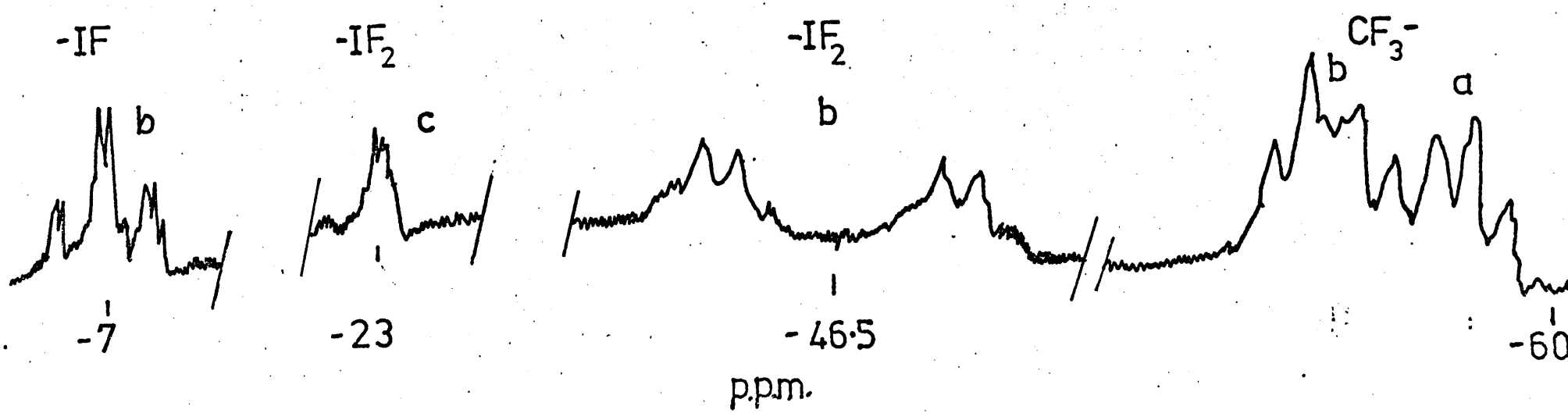
a = CF_3IF_4

b = CF_3IF_3OMe

c = $CF_3IF_2(OMe)_2$

Fig. 5b.

-80°C

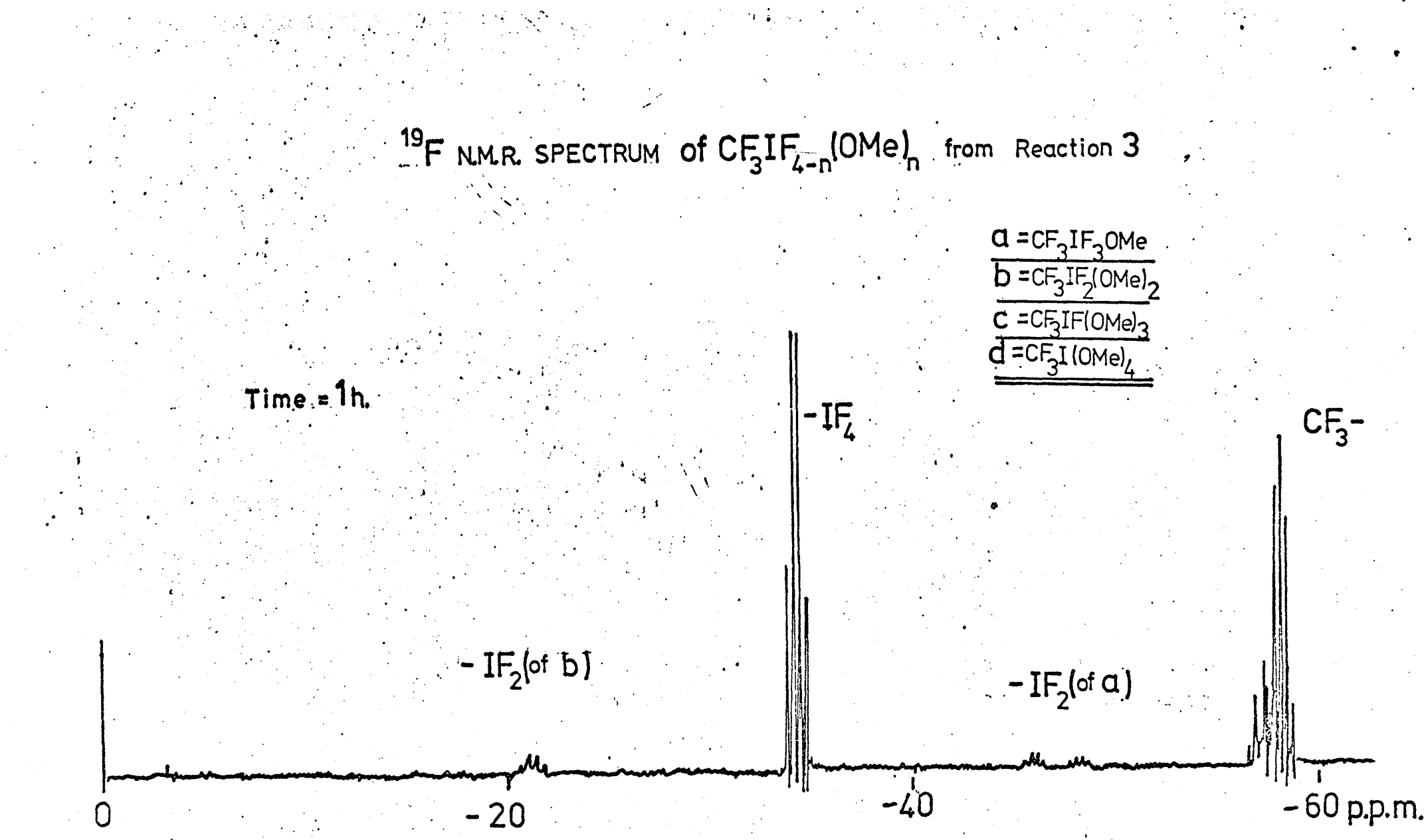


and their i.r. spectra, by comparison with the spectra of CF_3IF_4 and $IF_{5-n}(OMe)_n$, provide additional support.

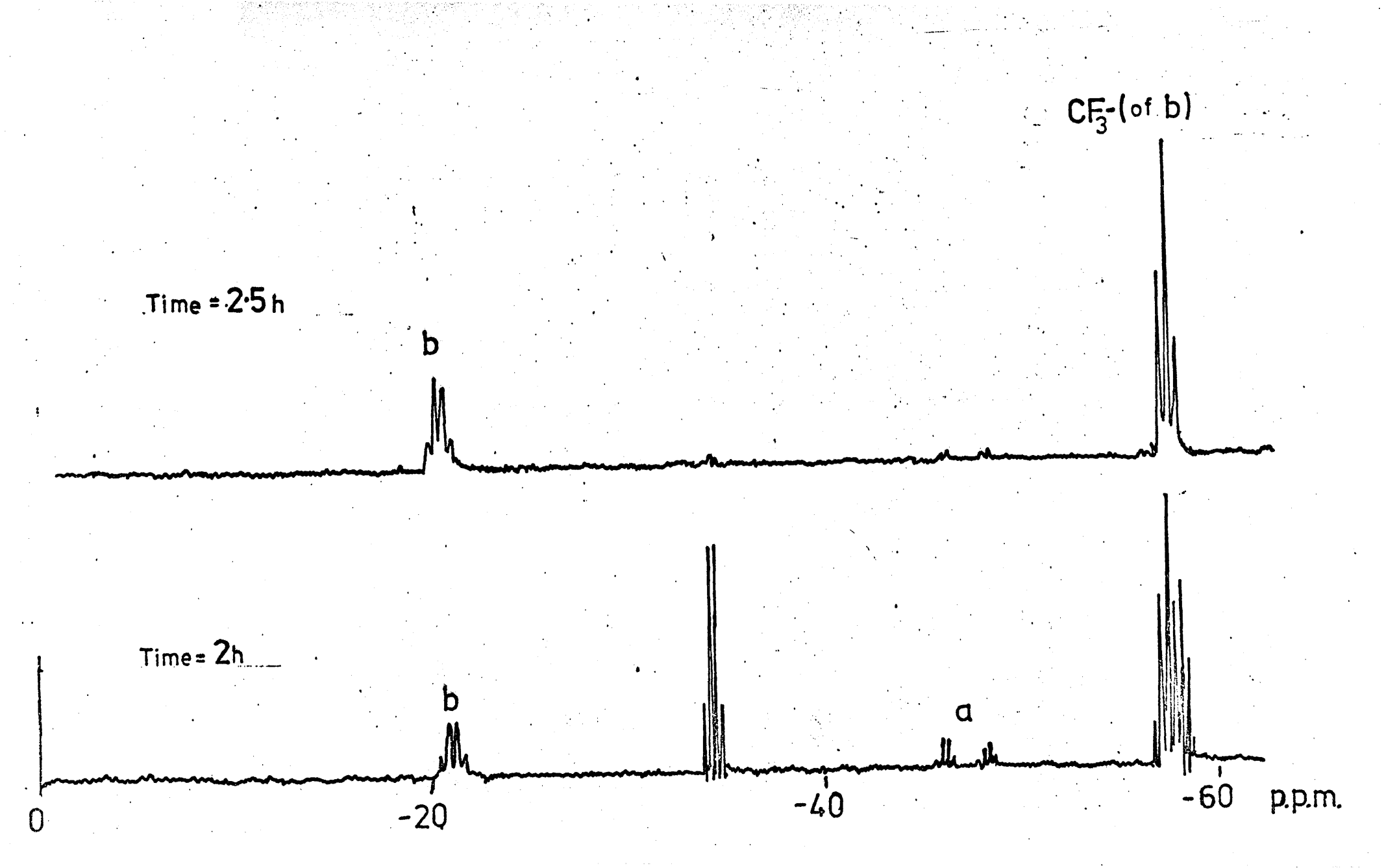
The rates of individual OMe - for -F substitutions are very different. For example, the 1:1 reaction (reaction 1, Table 6) is complete after 0.5h at 20°C, but quantitative formation of $CF_3I(OMe)_4$ is not achieved even after 9h. The course of reactions 3 and 4 was followed by recording their ^{19}Fn.m.r. spectra after various times. Only in reaction 3 were coupling constants observed at 20°C. After approximately 7 hours, the sample was cooled to -196°C and, upon reheating, the coupling was not observed at 20°C but was detected at -20°C. The presence of coupling at 20°C may indicate the high purity of the sample.

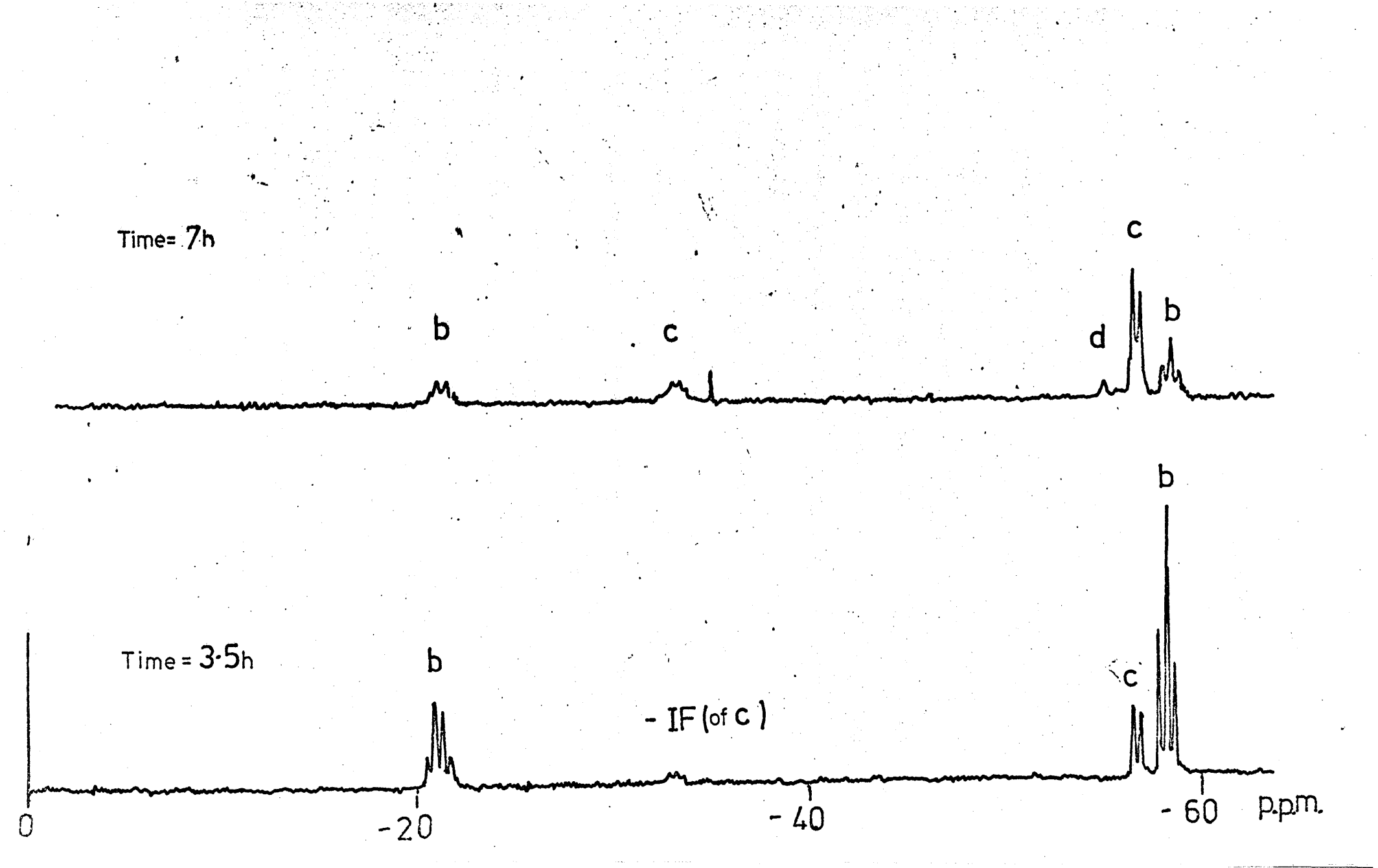
Separate ^{1}H signals due to chemically different OMe groups in products 1, 3 and 4 are not observed, either due to rapid exchange between species, or because of very small chemical shift differences. However, a ^{1}H - ^{19}F double resonance experiment on product 4 indicates the presence of a very small ^{1}H - ^{19}F coupling in $CF_3I(OMe)_4$.

Assignment of the ^{19}Fn.m.r. spectra is straightforward except for the signals in product 1 due to $CF_3IF_3(OMe)$ which are temperature dependent. Fig. 5a shows the ^{19}Fn.m.r. spectrum of product 1 at 20°C. Although stoicheiometric quantities were used in the reaction, there are significant amounts of CF_3IF_4 (δ-33.4 and -57.6p.p.m.) present in the final product. Fig. 5b shows the spectrum of product 1 at 80°C. A new triplet of quartets at δ -7.0p.p.m. is observed. A signal, which is thought to be a quartet, is observed at δ -23.3p.p.m. The signals at δ-33.4 and -57.6p.p.m. are still present. The broad peak observed at δ-46.9p.p.m. in the 20°C spectrum is a doublet of quartets at -80°C. The triplet at δ-56.6p.p.m. in the 20°C spectrum is a doublet of triplets, further complicated, as it overlaps with another


^{19}F N.M.R. SPECTRUM of $CF_3IF_{4-n}(OMe)_n$ from Reaction 3
a = CF_3IF_3OMe
b = $CF_3IF_2(OMe)_2$
c = $CF_3IF(OMe)_3$
d = $CF_3I(OMe)_4$
Time = 1h.
$-IF_4$
CF_3-
$-IF_2$(of b)
$-IF_2$(of a)
0
-20
-40
-60 p.p.m.

Fig


CF3-(of b)
Time = 2·5 h
b
Time = 2h
b
a
0
-20
-40
-60
p.p.m.


Time= 7h
b
c
d
c
b
Time = 3·5h
b
c
b
- IF (of c)
0
-20
-40
-60
p.p.m.

CF_3 signal. The signals have been assigned as shown in table 6. Hence at -80°C, a complete A_3M_2X spectrum is observed, whereas at 20°C neither the F_X signal nor F_A-F_X coupling in the F_A signal is observed. In this experiment, F_A-F_M coupling is not observed in the F_M signal at 20°C but is observed in the F_A signal. Thus the unique F atom of the $-IF_3$ group undergoes intermolecular exchange more readily than the other two, and is possibly subject to more efficient quadrupolar relaxation by ^{127}I.

The ^{19}Fn.m.r. spectrum of $CF_3IF_2(OMe)_2$ is two broad singlets, width at half-ht δ_A = 20 Hz , δ_X = 65Hz, at 20°C. At -80°C these signals resolve into a quartet δ_X-21.9p.p.m. assigned to the IF_2 group, and a triplet δ_A - 58.3p.p.m. assigned to the CF_3 group; that is an A_3X_2 spectrum.

The ^{19}Fn.m.r. spectrum of reaction 3 (Fig. 6) is more informative, as coupling is observed at 20°C. After 1h at 20°C CF_3IF_3OMe and $CF_3IF_2(OMe)_2$ in addition to CF_3IF_4 are observed. The low field signal due to the unique fluorine of CF_3IF_3OMe is not observed although F_M-F_X coupling is observed. Both CF_3IF_3OMe and $CF_3IF_2(OMe)_2$ continue to increase at the expense of CF_3IF_4, the maximum concentrations of CF_3IF_3OMe being observed ca. 1.5h after it is first detected, thus substantiating the presence in reaction 1 of $CF_3IF_2(OMe)_2$ and CF_3IF_4 in addition to CF_3IF_3OMe. Thereafter, $CF_3IF_2(OMe)_2$ increases at the expense of both CF_3IF_4 and $CF_3IF_3(OMe)$, and after a further 1h is the only species observed. Additional substitution occurs very slowly and after a further 3.5h the ratio of $CF_3IF(OMe)_3$: $CF_3IF_2(OMe)_2$ is ca. 2:1. At this time a low intensity signal, δ -54.8p.p.m., assigned to $CF_3I(OMe)_4$ and a sharp signal at δ -35.0p.p.m., which is thought to be due to a decomposition product, are also observed. After another hour the ratio of $CF_3I(OMe)_4$: $CF_3IF(OMe)_3$: $CF_3IF_2(OMe)_2$

is approximately 1:5:1. The products then decompose quickly, until after another hour two signals only are observed, δ -6-6p.p.m. assigned to CF_3I, and δ -35.0p.p.m. previously observed.

Similar results are obtained in experiment 4, except that no coupling is observed at 20°C and after ca. 10h only $CF_3I(OMe)_4$ is observed. The product quickly decomposes to give signals at δ -6.1p.p.m. assigned to CF_3I, and two unassigned signals at δ -76.1 and -77.2 p.p.m.

In reactions 3 and 4 it can be seen that the chemical shift of the CF_3 group moves to lower field as the degree of substitution increases. In reaction 3, the chemical shift decreases in steps of 1.4 p.p.m. in going from $CF_3IF_2(OMe)_2$ to $CF_3IF(OMe)_3$ to $CF_3I(OMe)_4$. The steps are 1.7 p.p.m. in reaction 4. δ (CF_3) of CF_3IF_4 and CF_3IF_3OMe cannot be distinguished as they overlap. The chemical shifts of the fluorine ligands do not move regularly. If it is assumed that $CF_3IF_{4-n}(OMe)_n$ have square pyramidal structures with axial CF_3 groups and F and OMe ligands in equatorial positions, it is reasonable to expect that replacement of F by OMe would have a regular effect on the chemical shift of the CF_3 group, as these ligands are cis to the CF_3 group. However, F ligands can have OMe in cis or trans positions. It has been shown that the chemical shifts of ^{19}F nuclei in substituted hexafluoro - stannates $(SnF_{6-n}X_n)^{2-}$, relative to SnF_6^{2-}, can be represented with some success by the equation $\delta(F) = pC + qT$, where $\delta(F)$ is the chemical shift of the fluorine in question relative to SnF_6^{2-}, p and q are the number of substituents cis and trans to the fluorine atom respectively, and C and T are empirical constants characteristic of substituent X. Although the systems dealt with here are square pyramidal it is interesting to compare the results[145]. C and T are calculated from CF_3IF_3OMe and applied to the other derivatives (Table 7).

TABLE 7

Comparison of experimental with calculated ^{19}F chemical shifts.

Compound	Experimental chemical shifts (p.p.m.)[a]		Calculated chemical shifts (p.p.m.)[b]	
	F_C	F_T	F_C	F_T
CF_3IF_3OMe	13.1	26.4	13.1	26.4
(cis F)			13.1	
$CF_3IF_2(OMe)_2$	11.5			
(trans F)			26.4	
$CF_3IF(OMe)_3$	0.1		0.1	

a. From CF_3IF_4, using the relationship $\delta(IF_4) = \delta(CCl_3F) + 33.4$ p.p.m.

b. Using the relationship $\delta_{(F)} = pC + qT$; for OMe C = 13.1 and T = -26.4 calculated from CF_3IF_3OMe.

c. F_C = fluorine cis to OMe; F_T = fluorine trans to OMe.

Good agreement is obtained for $CF_3IF(OMe)_3$. For $CF_3IF_2(OMe)_2$, where two structures are possible, reasonable agreement is obtained for a structure having cis OMe groups.

Having assumed axial CF_3 groups, the structures of CF_3IF_3OMe, $CF_3IF(OMe)_3$ and $CF_3I(OMe)_4$ follow. In the former two compounds the unique fluorine atom must be trans to an OMe group. However, two structures having cis or trans OMe groups are possible for $CF_3IF_2(OMe)_2$ (Fig. 7 a and b).

Fig. 7.

The $\delta(IF_2)$ value, discussed above, is more consistent with the former isomer, which would also be favoured on statistical grounds. It is noteworthy that the ^{19}Fn.m.r. spectra of $WF_4(OMe)_2$[123] and $TeF_4(OMe)_2$[122] have both been interpreted in terms of cis isomers.

The i.r. spectra of these products are consistent with the presence of CF_3 and OMe groups. The bands around 500 cm^{-1} are broad, except in $CF_3IF(OMe)_3$ when two bands are clearly observed at 520 cm^{-1} and 446 cm^{-1}. These bands cannot be unambiguously assigned, but the higher frequency band may be due to an I-F stretch and the lower, broader band to I-O stretch, although it may not be valid to separate the modes in this manner.

The mass spectra of $CF_3IF_{4-n}(OMe)_n$ (Table 8) show qualitative differences with increasing substitution; for example, the base peak in products 1 and 2 is $^{m}/_{e}$ = 69 assigned to CF_3^+, and in products 3 and 4 is $^{m}/_{e}$ = 29, assigned to CHO^+. Parent ions were not observed but peaks attributable to M-69, M-31 or M-19 are present. In product 2, $^{m}/_{e}$ = 277 and 265 are assigned to $CF_3IF(OMe)_2^+$ and $CF_3IF_2(OMe)^+$ respectively; in product 3, $^{m}/_{e}$ = 289 and 239 are assigned to $CF_3I(OMe)_3^+$ and $IF(OMe)_3^+$ respectively and in product 4, $^{m}/_{e}$ = 251 is assigned to $I(OMe)_4^+$. Some assignments are ambiguous due to the identical mass numbers of OMe and CF, but they are reasonable in view of the likely order of bond energies and the mass spectrum of CF_3IF_4.

Unlike the mass spectrum of CF_3IF_4 the spectra of these compounds contain ions in which iodine, bound to CF_3, has three other ligands, for example, in product 1, $^{m}/_{e}$ = 265, $CF_3IF_2(OMe)^+$ and in product 2, $^{m}/_{e}$ = 277, $CF_3IF(OMe)_2^+$ whereas in CF_3IF_4 only CF_3IF^+ is detected. The OMe group may stabilise these positive ions. In the spectra of $IF_{5-n}(OMe)_n$, many ions are observed which contain more fluorines than expected. All the spectra, but that of $CF_3IF_2(OMe)_2$, are of

TABLE 8

Mass spectra of involatile liquids for the reactions of CF_3IF_4 with methyl(methoxo) silanes.

m/e	Relative Abundance	Assignment[b]	m/e	Relative Abundance	Assignment[b]
		1. Mole ratio CF_3IF_4 : (OMe) = 1:1			
265	< 1	$CF_3IF_2OMe^+$	165	10	IF_2^+
227	3	CF_3IOMe^+	158	7	$IOMe^+$ CFI^+
215	2	CF_3IF^+ IF_3OMe^+	146	10	IF^+
196	39	CF_3I^+ IF_2OMe^+	127	56	I^+
			69	100	CF_3^+
189	2	$I(OMe)_2^+$	31	85	OMe^+ CF^+
184	1	IF_3^+	29	56	OCH^+
177	23	$IFOMe^+$ CF_2I^+			
		2. Mole ratio CF_3IF_4 : (OMe) = 1:2			
277	1	$CF_3IF(OMe)_2^+$	177	51	$IFOMe^+$ CF_2I^+
265	1	$CF_3IF_2OMe^+$	165	17	IF_2^+
227	23	CF_3IOMe^+	158	9	$IOMe^+$ CFI^+
215	3	CF_3IF^+ IF_3OMe^+			

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
196	94	CFI^+	157	3	$IOCH_2^+$
		IF_2OMe^+	146	17	IF^+
195	6	$IF_2OCH_2^+$	127	71	I^+
189	6	$I(OMe)_2^+$	69	100	CF_3^+
184	1	IF_3^+	31	65	OMe^+
					CF^+
			29	77	OCH_3^+
		3. Mole ratio CF_3IF_4 : (OMe) = 1:3			
289	< 1	$CF_3I(OMe)_3^+$	177	28	$IFOMe^+$
					CF_2I^+
277	3	$CF_3IF(OMe)_2^+$	165	5	IF_2^+
239	3	$IF(OMe)_3^+$	158	20	$IOMe^+$
					CFI^+
265	11	CF_3IOMe^+			
		$IF_2(OMe)_2^+$	157	6	$IOCH_2^+$
215	1	CF_3IF^+	146	8	IF^+
		IF_3OMe^+	127	69	I^+
196	37	CF_3I^+			
		IF_2OMe^+	69	79	CF_3^+
195	2	$IF_2OCH_2^+$	31	63	OMe^+
					CF^+
189	14	$I(OMe)_2^+$	29	100	OCH^+

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		4. Mole ratio CF_3IF_4 : (OMe) = 1:4			
289	<1	$CF_3I(OMe)_3^+$	177	13	$IFOMe^+$ CF_2I^+
277	<1	$CF_3IF(OMe)_2^+$	165	<1	IF_2^+
251	<1	$I(OMe)_4^+$			
			158	19	$IOMe^+$ CFI^+
239	1	$IF(OMe)_3^+$			
			157	7	$IOCH_2^+$
227	4	$IF_2(OMe)_2^+$	146	2	IF^+
		$CF_3IF(OMe)_2^+$	127	41	I^+
196	25	CF_3I^+ IF_2OMe^+	69	31	CF_3^+
189	3	$I(OMe)_2^+$	31	100	OMe^+ CF^+
			29	100	OCH^+

b Some cases are ambiguous due to the identical mass numbers of CF and OCH_3. Assignments made are those which appear to be most reasonable.

mixtures of the desired product and lower substituted derivatives, so that comparison with the spectra of $IF_{5-n}(OMe)_n$ is not valid. However, the mass spectrum of $CF_3IF_2(OMe)_2$, which from its ^{19}Fn.m.r. spectrum is free from $CF_3IF_3(OMe)$, contains ions at $^{m}/_{e}$ = 215, and 184 which can be assigned to IF_3OMe^+ and IF_3^+.

The ^{19}Fn.m.r. spectral observations strongly imply that $CF_3IF_3(OMe)$ undergoes a redistribution reaction according to equation

$$2CF_3IF_3(OMe) \rightarrow CF_3IF_4 + CF_3IF_2(OMe)_2 \qquad 16$$

This is consistent with the faster exchange observed for the fluorine ligand <u>trans</u> to OMe. This redistribution may be rationalised by the following scheme.

$$CF_3IF_3OMe \rightleftharpoons CF_3IF_2OMe^+ + F^- \qquad (i)$$

$$CF_3IF_3OMe + F^- \rightleftharpoons CF_3IF_4OMe^- \qquad (ii)$$

$$CF_3IF_4OMe^- \longrightarrow CF_3IF_4 + OMe^- \qquad (iii)$$

$$CF_3IF_2OMe^+ + OMe^- \longrightarrow CF_3IF_2(OMe)_2 \qquad (iv)$$

The species may not be ionic but the charges indicate the direction of polarisation. The initial transfer of fluorine may involve a fluorine bridged dimer in which the fluorine <u>trans</u> to OMe forms the bridge.

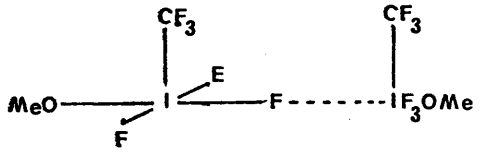


Fig. 8.

At 20°C the species observed in the ^{19}Fn.m.r. spectrum of product 2 may be more accurately described as $CF_3IF_2OMe^+$, F^-, and $CF_3IF_4^+$ and OMe^-. If the lone pairs on oxygen are donated to iodine, perhaps into the d orbitals, $CF_3IF_2OMe^+$ may be a relatively stable ion, whereas $CF_3IF_4OMe^-$ is probably very unstable due to steric crowding

around the nominally seven coordinate iodine. Due to the proposed stability of $CF_3IF_2OMe^+$, and slower exchange of OMe, reaction (iv) may be relatively slow. Hence $CF_3IF_2(OMe)_2$ is not observed at 20°C and only in small quantities at -80°C.

Due to this faster exchange observed for the unique fluorine in $CF_3IF_3(OMe)$, a trans configuration might be expected for $CF_3IF_2(OMe)_2$. A cis configuration has already been postulated but an unambiguous decision between the two is not possible. However, $CF_3IF_2(OMe)_2$ may have a cis configuration with the trans isomer being a possible intermediate in its formation. If $CF_3IF_2(OMe)_2$ has cis fluorines then these fluorines must be trans to OMe and by analogy with CF_3IF_3OMe both these fluorines should be labile. This may explain the lack of fine structure in the 20°C - ^{19}Fn.m.r. spectrum. Slow exchange of OMe ligands would explain the fact that a variety of products is not observed.

In the ^{19}Fn.m.r. spectrum of product 3, a signal assigned to $CF_3I(OMe)_4$ appears ca. 2 hours after $CF_3IF(OMe)_3$ is first detected. This product may arise from a redistribution process similar to that in CF_3IF_3OMe.

$$CF_3IF(OMe)_3 \longrightarrow CF_3IF_2(OMe)_2 + CF_3I(OMe)_4 \qquad 17.$$

Applying the argument that F trans to OMe is labile to the alkoxo-iodine(V) fluorides, their spectra may be better understood, particularly the ^{19}Fn.m.r. spectra of $IF_3(OMe)_2$ and $IF_3(OMe)(OEt)$, in which a redistribution of ligands has already been postulated, IF_4OR (R = Me, Et) arising from exchange of F for OR in $IF_3(OR)_2$. If the fluoride, alkoxides are fluorine bridged polymers a mechanism exists for this exchange. No $IF_2(OR)_3$ is observed in these spectra, suggesting that intermolecular exchange of OMe ligands is also slow in these systems. No intramolecular exchange has been proposed for

$CF_3IF_{4-n}(OMe)_n$ as the evidence is consistent with an axial CF_3 group, but there is no reason to suggest that intramolecular exchange of ligands does not also occur in $IF_{5-n}(OMe)_n$. Such a process would make identification of individual isomers more difficult.

Formation of fluorine bridges promoted by trans OMe ligands makes the formation of ions in the mass spectra of $IF_{5-n}(OMe)_n$, containing more fluorines than expected, reasonable. These compounds may, in fact, exist as fluorine bridged polymers in the liquid and solid phases.

This discussion has implied that alkoxo-iodine(V) fluorides may be polymeric and fluorine bridge polymers have been emphasised. I-F...I contacts have already been discussed for IF_5 and a crystal structure of IOF_3[51] has shown that many intermolecular I..F contacts are considerably less than the sum of the Van der Waals radii, indicating the likelihood of strong intermolecular attractions. However, in KIO_2F_2, it has been reported[146] that iodine has close intermolecular contacts with two oxygen atoms (I...O, 2.81A° and 2.89A°). Similarly, in I_2O_5, the iodine atoms form secondary bonds to oxygen such that they have pseudo-octahedral co-ordination[147]. In view of this, formation of oxygen bridged polymers in alkoxoiodine(V) fluorides cannot be excluded.

III Reaction of Iodine Pentafluoride with other Organosilicon compounds

Trimethylchlorosilane.

IF_5 reacts with Me_3SiCl at -45°C or above, producing Me_3SiF and a yellow solid, volatile at -25°C, which decomposes rapidly at or below ambient temperatures, the products being IF_5, I_2, Cl_2 and ICl or ICl_3. The yellow solid is thought to be IF_4Cl. It is soluble in CH_3CN and pyridine but in CH_3CN only signals due to IF_5 are observed at 20°C. In pyridine a signal at δ + 7 p.p.m. is observed, and a stable

yellow complex is isolated from solution. This adduct is soluble in IF_5. The ^{19}Fn.m.r. spectrum of this solution contains one signal at δ + 22.1 p.p.m., which is the chemical shift of IF_5 (singlet) observed in the ^{19}Fn.m.r. spectrum of a pyridine, IF_5 solution. It is noteworthy that no stable adduct can be isolated from this solution. The infrared spectrum of the pyridine complex is similar to that for PyICl.

Its analysis indicates that it contains chlorine and it may be a mixture of several pyridine adducts like PyICl, $PyICl_3$, $PyIF_5$ etc.

The yellow solid observed as an intermediate in the reaction between $N(Et)_4Cl$ and IF_5 has been formulated as IF_4Cl[66] and the chlorofluorides of I(III)[65] are yellow but these compounds have not been fully characterised. However, if IF_4Cl is formed and decomposes in a similar manner to CF_3IF_4, the expected products would be IF_5, IF_3, I_2, ICl and ClF. ClF has not been observed but it is known to react with iodine, although the products are not well characterised[1].

Hexamethyldisiloxane.

IF_5 reacts with $(Me_3Si)_2O$ between -80°C and room temperature to give several products. The volatile products are HF, Me_3SiF and possibly Me_2SiF_2. Elemental iodine is also produced. The infrared spectrum of the involatile liquid, is similar to that obtained for the alkoxo-iodine(V) fluorides. An additional band at 689 cm^{-1} may be due to an I=O stretch. The reaction was designed to produce IOF_3, and although IOF_3 may be formed the presence of iodine suggests that reduction of I(V) also occurs.

Trimethylpentafluorophenoxosilane.

A slow reaction occurs between IF_5 and $Me_3SiOC_6F_5$ at 20°C producing detectable quantities of Me_3SiF after three days. No other products are observed.

Trimethyl -1, 1, 1, 3, 3, 3 - hexafluoroisopropoxosilane and Trimethyl - 2-(1, 1, 1, 3, 3, 3 - hexafluoroisopropoxo) - hexafluoroisopropoxosilane.

No Me_3SiF is observed in the reaction between IF_5 and a mixture of $Me_3SiOCH(CF_3)_2$ and $Me_3SiOC(CF_3)_2OCH(CF_3)_2$ after 3 days. However, the ^{19}Fn.m.r. spectrum contains two low intensity signals at δ -5, and -76 p.p.m. The peak at δ -5 p.p.m. may indicate a substituted derivative of IF_5 is formed and the signal at δ -76 p.p.m. is indicative of a CF_3 group and is not attributable to either of the hexafluoroisopropoxo silicon compounds above. The most significant feature of this spectrum is the collapse of fine structure on the IF_5 resonances. After 2 weeks at 20°C, the ^{19}Fn.m.r. spectrum indicates two new signals attributable to Me_2SiF_2 (δ -133 p.p.m.) and Me_3SiF (δ -153 p.p.m.), thus implying that a very slow reaction is occurring

Methyltrimethylsilyl sulphide

IF_5 reacts with Me_3SiSMe exothermically below room temperature. The products include Me_3SiF, I_2, HF and possibly sulphur. SOF_2 is also produced. It is probably formed by hydrolysis of SF_4. The signal at δ -164 p.p.m., assigned to IF_3, grows at the expense of IF_5 in the ^{19}Fn.m.r. spectrum of the reaction mixture. The results suggest that, if a compound IF_4SMe is formed, it readily decomposes accompanied by oxidative fluorination of the sulphur and reduction of iodine.

Diethylaminotrimethylsilane.

As an IF_5, Me_3SiNEt_2 mixture detonated at low temperatures, attempts to prepare iodine(V) fluorides with N- containing ligands were abandoned. A compound IF_4NR_2 might decompose similarly to IF_4OR to form R_2NF. Nitrogen fluorides are known to be potentially hazardous substances. However, if the reaction were moderated by using a solvent, N- containing derivatives of IF_5 might be obtained, although they would have to be handled with extreme caution.

Discussion of Reactions

It has been proposed[148] that cleavage of silicon-element bonds by Lewis acids proceeds by an S_N2 mechanism via a weak four-centre transition state. For reactions involving IF_5, the following transition state can be visualised:

(I)

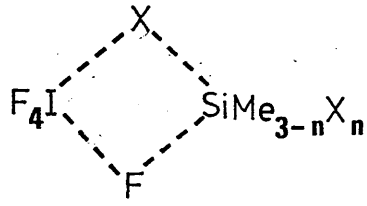


Fig. 9.

in which a lone pair of electrons on X donates to iodine. (X in this discussion is OR, SR, NR_2 or Cl) The ability of IF_5 to form weak donor-acceptor complexes has been observed (Introduction), and the difference in Si-F and Si-X bond energy terms (Table 1) contributes to the thermodynamic feasibility of the reactions.

When X = OMe or OEt, the formation of alkoxoiodine(V) fluorides from I can easily be visualised. The formation of I must depend, not only on the acceptor ability of IF_5, but also on the donor ability of X. Nitrogen is regarded as a better electron donor than oxygen and this may, in part, explain the violent reaction which occurs. Sulphur is also a better nucleophile than oxygen. However the ionization potential of sulphur is lower than that of oxygen[78], and oxidation of the sulphur occurs. Chlorine is a weak nucleophile but the formation of $WF_{6-n}(Cl)_n$ has also been discussed in terms of an S_N2 displacement at tungsten by Me_3SiCl[130].

The cleavage of the Si-O-Si bridge in hexamethyldisiloxane by IF_5 may follow the pathway:

$$IF_5 + (Me_3Si)_2O \longrightarrow \underset{(II)}{[IF_5O(SiMe_3)_2]} \longrightarrow \underset{(III)}{[IF_4OSiMe_3]} + Me_3SiF$$

II may be a four-centre type complex as above I. By analogy with other systems, III would be expected to decompose to IF_3O and Me_3SiF

$$Me_3Si\text{—}O\text{—}I(F_3)\text{—}F \longrightarrow O=IF_3 + Me_3SiF$$

However, the formation of an iodine-oxygen double bond by this process does not appear to be favourable. Due to increased oxygen-to-silicon $(p\rightarrow d)\pi$ bonding, siloxanes are weaker donors than alkoxosilanes[131], and generally react more slowly. It may be, therefore, that side reactions, such as those observed in the IF_5/fluorosilane reactions below, occur to further complicate the reaction.

The reaction between IF_5 and $Me_3SiOC_6F_5$ proceeds only very slowly probably because of the effect of the C_6F_5 group. The electron density on oxygen can be decreased both by the inductive effect of the C_6F_5 group and by resonance stabilisation around the ring. Attack of the lone pair on iodine may also be sterically hindered by the bulky C_6F_5 group. The inductive effect of the CF_3 groups and steric hindrance may also be the cause of the slow reaction between IF_5 and the $Me_3SiOCH(CF_3)_2/Me_3SiOC(CF_3)_2OCH(CF_3)_2$ mixture. The loss of fine structure of IF_5 in the ^{19}Fn.m.r. spectrum of the reaction mixture suggests that exchange of fluorine ligands is taking place without replacement by an OR group. It may be that the species in solution is a complex of the type,

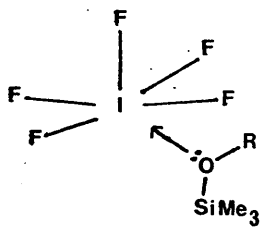


Fig. 10.

in which weak coordination of the oxygen promotes intermolecular fluorine exchange, similar to that observed in CH_3CN/CF_3IF_4, C_5H_5N/CF_3IF_4 or C_5H_5N/IF_5 systems. Such a complex may be the initial step in the formation of the four centre transition state I.

The rate of substitution of OMe for F in IF_5 and CF_3IF_4 decreases with increasing numbers of OMe bound to iodine, and this may be

due to both the steric effect of the OMe groups and a reduction in the acceptor ability of iodine.

IV The Reaction of Iodine Pentafluoride with Trimethylsilyl Trifluoroacetate and Trimethylsilyl Acetate.

(i) Trimethylsilyl Trifluoroacetate.

IF_5 reacts exothermically with $Me_3SiOC(O)CF_3$ at 20°C. The reaction proceeds in two stages, the final products being IF_5, Me_3SiF and Me_2SiF_2, identified by their n.m.r. spectra; $CF_3C(O)F$ and $CH_3OC(O)CF_3$ identified by infrared spectroscopy. A low intensity signal in the ^{19}F.n.m.r. spectrum of the reaction mixture at δ-6 p.p.m. is thought to indicate the presence of a substituted derivative of IF_5. A strong signal, at δ-78 p.p.m. in the ^{19}Fn.m.r. spectrum and a singlet in the ^{1}H spectrum, δ 3.7 p.p.m., are assigned to $CH_3OC(O)CF_3$. A low intensity signal at δ 4.3 p.p.m. in the ^{1}Hn.m.r. spectrum remains unassigned.

(ii) Trimethylsilyl Acetate.

IF_5 reacts rapidly with $Me_3SiOC(O)CH_3$ at the melting point of IF_5(10°C). The products, the relative amounts of which depend on the reaction stoicheiometry, are a black solid, an involatile viscous liquid and several volatile products. The black solid is thought to be iodine The infrared spectrum indicates that the liquid product contains I-F and possibly I-O bonds. C-H and C=O bonds are also indicated. A mass spectrum of this substance contained peaks attributable to IF_5, IF_4OCH_3 $CH_3C(O)F$, methyl acetate and other species. The volatile products include Me_3SiF, Me_2SiF_2 and $CH_3C(O)F$. The presence of methyl acetate was supported by signals in the ^{1}Hn.m.r. spectrum of the reaction mixture at δ 1.8 and 3.3 p.p.m.

The reaction of $Me_3SiOC(O)CH_3$ with approximately one equivalent of IF_5, produced several products, observed in the ^{1}Hn.m.r. spectrum of the reaction mixture, which were not observed in the previous

reaction and could not be identified. The ^{19}Fn.m.r. spectrum of the volatiles obtained from this reaction, contains a peak at δ -168 p.p.m. which was not previously observed, and is tentatively assigned to IF_3 or a derivative thereof.

Discussion of Trimethylsilyl acetate reactions.

In view of previous reactions with organosilicon ethers, it seems reasonable to propose that $IF_4OC(O)R$ (R = Me, CF_3) is initially formed, possibly via an IF_5: $Me_3SiOC(O)R$ complex, according to the equation:

$$IF_5 + Me_3SiOC(O)R \longrightarrow IF_4OC(O)R + Me_3SiF \quad 18.$$

Neither of the products proposed are observed in good yield. Further reaction between these two species could produce Me_2SiF_2 and $MeOC(O)R$:

$$IF_4OC(O)R + Me_3SiF \longrightarrow IF_3 + Me_2SiF_2 + MeOC(O)R$$

or it may be formed from the action of IF_5 on Me_3SiF (Section V). IF_3 is known to decompose to IF_5 and I_2 but has been observed in previous reactions. Acetyl and trifluoroacetyl fluorides may be formed in the following reactions:

$$IF_4OC(O)R \longrightarrow IOF_3 + FC(O)R$$

$$\text{or } MeOC(O)R + IF_5 \longrightarrow IF_4OMe + FC(O)R \quad 19.$$

If $IF_4OC(O)R$ decomposes in a similar manner to IF_4OR, IF_3 and $RC(O)OF$ would be produced. $RC(O)F$ has been assigned mainly on its C=O stretching frequency and this assignment must be considered tentative. A better understanding of the reaction scheme may be obtained by using stoicheiometric quantities of IF_5 and $Me_3SiOC(O)R$, as the IF_5 may react with the products formed. It may also be possible to follow the reaction by ^{19}F and ^{1}H n.m.r. spectroscopy, although low temperatures will be needed.

V The Reaction of Iodine Pentafluoride with Tetramethylsilane, Trimethylfluorosilane and Dimethyldifluorosilane.

Prompted by the observation of Me_2SiF_2 in some reactions of IF_5

with trimethylsilyl compounds, the following reactions were investigated.

IF_5 reacts with Me_4Si slowly at 20°C, producing Me_3SiF after 1-2 days and significant quantities of Me_2SiF_2 after 4 days. The other products which can be observed after 1-2 days are I_2 and SiF_4. From signals in the ^{19}F n.m.r. spectrum at δ -4.9 and -167 p.p.m. the other products appear to be a substituted derivative of IF_5 and IF_3 respectively.

IF_5 reacts slowly with Me_3SiF, such that after 7 days approximately a quarter of the Me_3SiF is converted to Me_2SiF_2.

The ^{19}F n.m.r. spectrum of a mixture of IF_5 and Me_2SiF_2 contained low intensity signals at δ -5.8 and -134 p.p.m. suggesting that an extremely slow reaction occurs to produce $MeSiF_3$, and possibly CH_3IF_4.

In a reaction between IF_4OMe and Me_3SiF, no Me_2SiF_2 is detectable even after 4 days. SiF_4 is produced, but this may be formed by attack of HF on the glass reaction vessel. SiF_4 in other reactions is also thought to arise from attack on the glass by HF rather than by the action of IF_5 on the fluorosilane.

It is difficult to differentiate the various methylfluorosilanes in an infrared spectrum of a mixture. They can, however, be unambiguously identified by their n.m.r. spectra (Table 9) and in particular by their ^{19}F chemical shifts.

TABLE 9

N.M.R. data on methylfluorosilanes.

Compound	$-\delta_F$ (p.p.m.)[149]	δ_H (p.p.m.)	J_{HF} (Hz)[149]
SiF_4	163		
CH_3SiF_3	135	1.0[150]	4
$(CH_3)_2SiF_2$	132	0.3[a]	6
$(CH_3)_3SiF$	159	0.2[a]	8
$(CH_3)_4Si$		0	

[a] relative to t.m.s. internal

They can also be identified from their mass spectra by their molecular ions(M^+), although coincidences in the fragment ions do occur.

M^+	SiF_4^+	$MeSiF_3^+$	$Me_2SiF_2^+$	Me_3SiF^+
m/e	104	100	96	92

The base peak in the spectra of the methylfluorosilanes corresponds to $(M-CH_3)^+$.

Methylfluorosilanes have no basic heteroatom, other than fluorine, to form a Lewis acid-base intermediate of the type previously discussed. The intermediate in these reactions probably involves donation of electrons from the σC-Si bond to the iodine prior to exchange of ligands, CH_3 for F. Charge transfer interactions between transition metal fluorides and Me_4Si have been observed, and the process is described as a transition to the metal from the σC-Si bond[151]. It is also believed that a synergic process is possible whereby the fluoride behaves as a donor to non-bonding orbitals localised on Si. This process suggests an intermediate of the type.

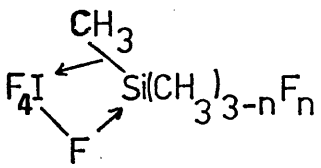


Fig. 11.

It can be seen that ease of replacement of CH_3 by F in methylfluorosilanes decreases in the order

$$(CH_3)_4Si > (CH_3)_3SiF > (CH_3)_2SiF_2$$

This can most simply be explained by the inductive effect of the

fluorines which would decrease the electron density in the Si-C bond thus making the formation of the above intermediate less likely. A reduction in reaction rate is also expected on statistical grounds.

Cleavage of Si-C bonds has been observed in reactions between AsF_5 and trimethylsilyl compounds[152]. In attempts to prepare derivatives of AsF_5, Me_2SiF_2 and only a few percent of Me_3SiF are formed. AsF_3 does not react with Me_3SiF, demonstrating that the exchange of F for CH_3 depends not only on the basicity of the Si-C bond but also on the Lewis acidity of the fluoride. In the reaction between AsF_5 and Me_3SiF, $MeSiF_3$, MeF and AsF_3 are formed. It seems likely that AsF_3 and MeF are formed in the disproportionation of CH_3AsF_4. A similar redistribution in CH_3IF_4 would produce IF_3 and MeF. IF_3 is detected in the ^{19}Fn.m.r. spectrum of the reaction between IF_5 and Me_4Si, but no MeF is observed. It may be that MeF if produced reacts further.

VI Reactions of Iodine Pentafluoride with Sulphite Esters.

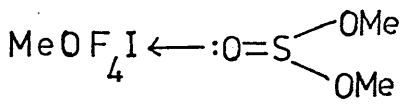
IF_5 and sulphite esters, $(RO)_2SO$(R = Me, Et), react at or slightly below room temperature with exchange of RO and F substituents.

$$IF_5 + (RO)_2SO \longrightarrow IF_4OMe + ROS(O)F \qquad 20.$$

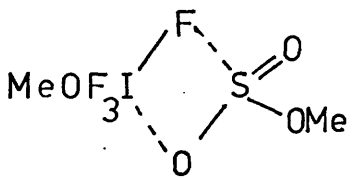
However, the reaction of iodine pentafluoride with $(PhO)_2SO$ yields only hydrolysis products, SO_2, SiF_4, I_2 and tar. IF_4OR are identified from their n.m.r. spectra by comparison with values in Table 4, and ROS(O)F have been previously reported[137, 139]. The addition of pyridine to an $IF_5/(MeO)_2SO$ mixture gives a white solid, the i.r. spectrum of which is similar to $C_5H_5N.IF_4OMe$.

With excess IF_5 and $(MeO)_2SO$, IF_4OMe and MeOS(O)F are observed, but with excess $(MeO)_2SO$, IF_4OMe and MeOS(O)F are produced only slowly and IF_5 and $(MeO)_2SO$ can still be detected after several days.

No n.m.r. signals due to $IF_3(OMe)_2$ are observed. The infrared spectrum of the liquid isolated from this reaction contains bands characteristic of a methoxoiodine(V) fluoride but there are extra bands at 1190 and 708cm^{-1} consistent with νS=O and νS-F[153]. Analysis of this material also suggests that methylfluorosulphite or dimethyl sulphite is complexed to the iodine fluoride. Similar results are obtained in the spectra from the $IF_5/(EtO)_2SO$ reaction. The reaction of WF_5OMe with dimethyl sulphite gives $WOF_4.OS(OMe)_2$ among other products[139]. In these reactions it may be that weak coordination of $(MeO)_2SO$ and/or MeOS(O)F to IF_4OR slows the reaction rate. If coordination is <u>via</u> the double-bonded oxygen atom, this may reduce the electron donating power of the oxygen bound to C and S inductively,



(a)



(b)

Fig. 12

making the formation of a four-centred transition state(b) less likely.

In reactions of IF_5 with sulphite esters, only one of the fluorine atoms in IF_5 is substituted and only one OR group of the sulphite ester is exchanged. This implies that the following reactions do not occur.

$$IF_5 + MeOS(O)F \longrightarrow IF_4OMe + SOF_2 \qquad 21.$$

$$IF_4OMe + (MeO)_2SO \longrightarrow IF_3(OMe)_2 + MeOS(O)F \qquad 22.$$

Neither SOF_2 nor $IF_3(OMe)_2$ are detected. This may be due, in reaction 21 to a reduction in the basicity of the remaining OMe group due to increased $(p \rightarrow d)\pi$ bonding in the MeO-S bonds, and in reaction 22 to a reduction in acidity of I(V) in IF_4OMe compared to IF_5, both of which would make the formation of a transition state like (b) less likely.

VII Reactions of Iodine Pentafluoride and Methoxoiodine(V) Tetrafluoride with Trimethyl Phosphite.

IF_5 reacts vigorously with trimethyl phosphite above $-80^{\circ}C$, and explosions can occur. The products of the reactions depend both on stoicheiometries and reaction temperature. Assignments of some of the n.m.r. signals obtained from the reaction mixtures are listed in Table 12, by comparison with literature values (Table 11).

In reaction (i) one product has been formulated as $(MeO)_3PMe^+ PF_6^-$. The anion could arise from fluorination of phosphorus and the cation via methylation of phosphorus by IF_4OMe. However, no evidence of this methylation process is observed in the reaction between IF_4OMe and $P(OMe)_3$. The chemical shifts of the "unknown" compound have been compared with those of Darragh, who identified a species tentatively formulated as $(MeO)_2PF_2OPF_2(OMe)_2$ in the reaction of SF_4 with $P(OMe)_3$[125].

The mass spectral data is consistent with the presence of $(MeO)_2P(O)F$ $m/e = 128$ confirming the n.m.r. spectral assignments. The ion at $m/e = 112$ is assigned to MeO(F)P(O)Me by comparison with spectra obtained by Darragh. However this species is not observed in the ^{19}Fn.m.r. spectrum and may arise in the mass spectrometer from $(MeO)_2P(O)F$ by a rearrangement process. It may also be formulated as the P(III) compound $P(OMe)_2F$. Similarly, the ion at $m/e = 100$ may be formulated as $P(OMe)F_2$ or $MeP(O)F_2$, neither of which are detected in the ^{19}Fn.m.r. spectrum of the reaction mixture. Several metastables

are observed for the fragmentation of the species formed, and loss of formaldehyde is an important rearrangement process. For example:

$$CH_3O\overset{F}{\underset{}{P}}(O)CH_3^{+} \xrightarrow[m^* = 60{\cdot}0]{-CH_2O^{\cdot}} CH_3\overset{F}{\underset{}{P}}(O)H^{+}$$

$m/e = 112$

CH_2O is formed by P-O bond cleavage and simultaneous hydrogen migration from carbon to phosphorus. Migration to phosphorus and not to oxygen is postulated because phosphorus is known to prefer a four coordinate structure with a P=O bond. The structure of, for example, the ion $^{m}/_{e}$ 82 is best represented as:

$$CH_3-\overset{F}{\underset{H}{P}}=O^{+}$$

Methyl elimination is also observed and this process has previously been shown to be a major fragmentation process in methyl phosphines[154] and trimethyl phosphite[155].

IF_5 is a much stronger fluorinating agent towards $P(OMe)_3$ than IF_4OMe and although the identification of the products is not unambiguous the spectral data are more consistent with the formation of P(V) compounds than P(III) derivatives. SF_4 reacts with $P(OMe)_3$ to give $PF_2(OMe)_3$[125] and it seems reasonable to propose that one of the compounds initially formed from IF_5 and $P(OMe)_3$ is also $PF_2(OMe)_3$. Alkoxofluorophosphoranes are thermally unstable and readily lose alkyl fluoride with the formation of phosphoryl compounds. Loss of methyl fluoride from $PF_2(OMe)_3$ would produce $(MeO)_2P(O)F$ according to:

$$PF_2(OMe)_3 \longrightarrow (MeO)_2P(O)F + MeF \qquad 23.$$

Tertiary phosphite esters are known to undergo valence shell expansion to give phosphorus(V) derivatives containing phosphoryl groups. This

process is known as the Michaelis-Arbuzov[156] rearrangement.

$$P(OMe)_3 + RX \rightleftharpoons [(MeO)_3 PR^+X^-] \rightarrow RP(O)(OMe)_2 + MeX \quad 24.$$

This rearrangement can occur in the presence of alkyl halides and organic polyhalides such as methylene bromide, carbon tetrachloride, haloethers, haloketones and halocarboxylic acid, and their derivatives. The phosphonium intermediate has been isolated in the reaction between triphenyl phosphite and methyl iodide. $(MeO)_2P(O)Me$ could arise from such a rearrangement. In this case RX would be MeI or MeF. Iodine may also take part in these reactions and this may explain the formation of MeI.

$$P(OMe)_3 + I_2 \rightleftharpoons [(MeO)_3PI^+I^-] \rightarrow (MeO)_2P(O)I + MeI \quad 25.$$

The reaction mixture may also contain compounds of type $P(O)_nI_n(OMe)_{3-n}$ $(n = 1, 2)$.

There is no evidence to suggest that exchange of F and OMe ligands to form IF_4OMe and $PF(OMe)_2$ is a major reaction pathway, as only traces of IF_4OMe are detected in reaction (i). However, it has been suggested that Me(O)P(F)OMe can be formed from $PF(OMe)_2$ <u>via</u> a Michaelis-Arbuzov rearrangement[157].

$$PF(OMe)_2 \longrightarrow MeP(O)F(OMe) \quad 26.$$

These reactions are obviously very complex and a complete analysis of the products would require more sophisticated techniques, for example, G.C.M.S.

CONCLUSIONS

The reactions of IF_5 and R_FIF_4 with methylalkoxosilanes involve exchange of F and OR substituents (R = Me, Et), and provide a route to $IF_{5-m}(OR)_m$ and $R_FIF_{4-n}(OMe)_n$. (m = 1-5; n = 1-4). IF_4OR can be isolated pure and appears to be monomeric in solution. Evidence suggests that the higher substituted derivatives are polymeric. $Me_2Si(OR)_2$ is the preferred reagent for these reactions, as IF_5 reacts with Me_3SiF. The Si-C bonds of Me_4Si and Me_3SiF are more readily cleaved by IF_5 than those of Me_2SiF_2. In some cases higher substituted derivatives of IF_5 appear to be mixtures. In particular, when m = 2, the mixture contains IF_4OR, $IF_3(OR)_2$ and possibly $IF_2(OR)_3$. Similarly, $R_FIF_3(OMe)$ disproportionates to R_FIF_4 and $R_FIF_2(OMe)_2$. The structure of $IF_{5-m}(OMe)_m$ (m > 1) have not been established but the ^{19}Fn.m.r. spectra of $R_FIF_{4-n}(OMe)_n$ are consistent with an axial R_F group and equatorial F and OMe groups. The thermal stabilities of $IF_{5-m}(OR)_m$ are in the order Me > Et and decrease as m increases. HF and possibly formaldehyde are produced in the decomposition. The reactions of IF_4OMe are consistent with its ability to lose Me^+ or F^-. It is a milder fluorinating reagent than IF_5.

The reactions of IF_5 with trimethylsilyl compounds, Me_3SiX, cleave the silicon element bond to form Me_3SiF. When X=Cl, IF_4Cl may be formed initially but it readily disproportionates below 20°C to IF_5, ICl, and other products. Similarly when X=OC(O)R (R = Me, CF_3), $IF_4OC(O)R$ may be formed but further reaction with IF_5 or decomposition of the derivative prevents its isolation. These reactions require further investigation. With $OSiMe_3$ & SMe groups, complicating side reactions occur and the desired I(V) derivative is not isolated. The data for the reactions of IF_5 with $Me_3SiOC_6F_5$, $Me_3SiOCH(CF_3)_2$/ $Me_3SiOC(CF_3)_2OCH(CF_3)_2$ mixture and $Me_3SiN(Et)_2$ are incomplete but indicate that the rate of reaction between IF_5 and organosilicon compounds

depends on the basicity of the hetero-atom and the bulkiness of the substituent.

The reactions of IF_5 with sulphite esters also involve exchange of F and OR ligands although excess sulphite may complex with the products. The reaction of IF_5 with trimethylphosphite is complex and the products are not well characterised, but it has been established that oxidative fluorination of P(III) to P(V) occurs.

Finally, it has not been possible to obtain phenoxo derivatives from reactions of IF_5 with either Me_3SiOPh or $(PhO)_2SO$ and it is thought that the phenyl ring is readily fluorinated.

EXPERIMENTAL

Chemicals

IF_5, prepared by the reaction of iodine with fluorine, or obtained from Fluorochem Ltd. was purified by trap to trap distillation at 20°C over NaF, and stored over NaF and Hg to remove I_2. Other reagents were obtained or prepared as in Table 10. They were purified by trap to trap distillation and stored over activated Linde 4A molecular sieves. AnalaR or spectroscopic grade solvents(B.D.H.) were used where available and stored over activated Linde 4A molecular sieves. C_6F_6(Imperial Smelting Co.) was purified by trap to trap distillation and stored over sodium.

Experimental Procedure.

Reactions were carried out in a conventional high-vacuum system. Rigorous precautions were taken to exclude moisture. A description of the reaction vessels and instrumentation has been given.

I Reactions of Iodine Pentafluoride with Alkoxomethylsilanes.

The conditions and products of the reactions of IF_5 with alkoxosilanes are summarised in Table 11. The n.m.r. spectra of $IF_{5-n}(OR)_n$ are summarised in Table 4, and the mass spectra in Tables 2 and 5. Descriptions of typical reactions are given below.

The Reactions of IF_5 with $Me_{4-n}Si(OMe)_n$ (n = 1, 2.)

(a) Preparation of IF_4OMe.

IF_5(1.62g., 7.3 m.mol) and Me_3SiOMe (0.75g, 7.2 m.mol.) were allowed to react at 20°C. Heat of reaction could be detected and after 30 mins. a colourless liquid was obtained. The volatile products, (Me_3SiF + trace IF_5 found 0.68 g, required 0.68g). were removed leaving a white solid.

IF_5 (2.39g, 10.8m.mol.) and $Me_2Si(OMe)_2$ (0.64g, 5.4 m.mol.) were allowed to react for 30 mins. at 20°C. The n.m.r. spectra of

TABLE 10

Chemical	Source
Me_3SiOMe	Pierce Chem. Co. or $Me_3Si\overset{H}{N}SiMe_3$ + MeOH[158]
$Me_2Si(OMe)$	Aldrich
Me_3SiOEt	Me_3SiCl + EtOH[159]
$Me_2Si(OEt)_2$	Alfa Inorganics Inc.
Me_3SiCl	B.D.H.
Me_3SiOPh	Me_3SiCl + PhOH[160]
$Me_3SiOSiMe_3$	Koch Light Lab. Ltd.
$Me_3SiOC_6F_5$	C_6F_5OH (Ralph N. Emmanuel Ltd.) + Me_3SiCl[161]
$Me_3SiOCH(CF_3)_2$ and $Me_3SiOC(CF_3)_2OCH(CF_3)_2$	Me_3SiH + $(CF_3)_2CO$[162] (both P.C.R.)
Me_3SiSMe	donated by D. W. Walker
$Me_3SiN(Et)_2$	Aldrich
$Me_3SiOC(O)CF_3$	Me_3SiCl + $Ag.OC(O)CF_3$(P.C.R.)[163]
$Me_3SiOC(O)CH_3$	Me_3SiCl + $Ag.OC(O)CH_3$(B.D.H.)[163]
Me_4Si	Aldrich
Me_3SiF	WF_6 + $Me_3SiN(Et)_2$
Me_2SiF_2	donated by Dr. A. Majid
$(MeO)_2SO$	Aldrich
$(EtO)_2SO$	Aldrich
$(PhO)_2SO$	$SOCl_2$ + PhOH[164]
$P(OMe)_3$	B.D.H.

TABLE 11

Reactions of IF_5 with methylalkoxosilanes

Reactants (m.mol.)	Reaction Conditions	Products identified
IF_5(4.5) + Me_3SiOMe(3.5)	20°C 30 mins.	IF_5 unreacted IF_4OMe[a], Me_3SiF Me_2SiF_2(trace)
IF_5(7.3) + Me_3SiOMe(7.2)	20°C "	IF_4OMe[a] Me_3SiF[a] + IF_5(trace)
IF_5(5.5) + Me_3SiOMe(5.4)	20°C "	IF_4OMe[a] Me_3SiF + IF_5(trace)
IF_5(10.8) + $Me_2Si(OMe)_2$(5.4)	20°C "	IF_4OMe[a] Me_2SiF_2
(b)IF_5(8.0) + Me_3SiOMe(15.7)	20°C 50 mins	$IF_3(OMe)_2$ + IF_4OMe Me_3SiF ratio 2:1[b]
IF_5(5.7) + $Me_2Si(OMe)_2$(5.6)	20°C 1h	$IF_3(OMe)_2$ + IF_4OMe[c] Me_2SiF_2
IF_4OMe(9.8) + Me_3SiOMe(9.8)	20°C 1hr. CH_3CN	$IF_3(OMe)_2$ + IF_4OMe[c] Me_2SiF_2
(c) IF_5(8.4) + $Me_2Si(OMe)_2$(12.5)	20°C 1½h. 1h.	$IF_2(OMe)_3$[a] Me_2SiF_2
(d) IF_5(10.9) + $Me_2Si(OMe)_2$(21.8)	20°C 2h.	$IF(OMe)_4$[a] Me_2SiF_2[a]
(e) IF_5(6.1) + Me_3SiOMe(31.6)	20°C 12h. shaking	$I(OMe)_5$ Me_3SiF
IF_5(6.5) + $Me_2Si(OMe)_2$(16.4)	20°C 2h.	$I(OMe)_5$[a] $IF(OMe)_4$[a] (trace) Me_2SiF_2
(f) IF_5(6.4) + Me_3SiOEt(6.3)	20°C 50 mins.	IF_4OEt[a] Me_3SiF
IF_5(6.0) + $Me_3Si(OEt)_2$(3.0)	20°C 20 mins.	IF_4OEt[a] Me_2SiF_2
(g) IF_5(3.3) + $Me_2Si(OEt)_2$(3.3)	20°C 15 mins.	$IF_3(OEt)_2$[c] Me_2SiF_2

Reactants (m.mol.)	Reaction Conditions	Products identified
(h) IF_4OMe(6.5) + Me_3SiOEt(6.2)	20^oC 30 mins. CH_3CN	$IF_3OMeOEt$[c] Me_3SiF

a identified by F n.m.r. and mass spectra

b ratio from ^{19}F n.m.r. spectrum and very approximate

c n.m.r. indicates a mixture

d fluorosilanes identified by n.m.r. mass and i.r. spectra

the reaction mixture showed that only IF_4OMe and Me_2SiF_2 were present. A white solid was isolated on removing the volatile material at 0°C. (Me_2SiF_2; found 0.51g, required 0.52g.)

The white solid was characterised as Methoxoiodine(V) Tetrafluoride, m.p. 35-7°C, by analysis (Found C, 5.4; H, 1.2%. CH_3F_4IO requires, C, 5.2; H, 1.3%) and by its mass spectrum. The identities of $IF_4OCH_2^+$ and $IF_3OCH_3^+$ were confirmed by mass measurement. Found 232.910 and 214.919; required 232.909 and 214.918. Its ^1H and ^{19}F n.m.r. spectra in IF_5, C_6F_6 and CH_3CN were singlets. Chemical shifts are presented in Table 3. Its i.r. spectrum (4,000 - 400 cm^{-1} nujol and fluorolube mulls) comprised peaks at 2970w, 2915sh, 1443w, 962s, 880m, 725w, 610sh, 560sbr, cm^{-1}. At attempt was made to determine the molecular weight of IF_4OMe by measuring the lowering of the vapour pressure of CH_3CN, but owing to slight hydrolysis of the sample, no reasonable results were obtained. The determination gave a value of 209, required 234. Although the result is not precise it indicates that IF_4OMe is monomeric in CH_3CN.

(b) Preparation of $IF_3(OMe)_2$

IF_5(1.78g 8.0 m.mol.) and Me_3SiOMe(1.64g, 15.7 m.mol.) were allowed to react at 20°C for approximately 1h. giving a colourless solution. The volatile product, Me_3SiF identified by its i.r. and mass spectra was removed, leaving a pale pink, slightly volatile liquid.

IF_5 (1.26g, 5.7 m.mol.) and $Me_2Si(OMe)_2$ (0.68g, 5.6 m.mol.) were allowed to react at 20°C for 1h. The products were Me_2SiF_2 and a colourless liquid.

IF_4OMe (2.30g, 9.8 m.mol.) and Me_3SiOMe (1.02g, 9.8 m.mol.) reacted in CH_3CN at 20°C to produce Me_3SiF and a colourless liquid. Dimethoxoiodine(V) trifluoride is a colourless liquid at 20°C. It was characterised by analysis. Found C, 9.1; H, 2.4, F, 21.0; I, 52.4% .

$C_2H_6F_3IO_2$ requires C, 10.0; H, 2.5; F, 23.2; I, 52.9%. Its n.m.r. and mass spectra have been listed in Tables 4 and 5 and suggest that the product is a mixture. The ^{1}Hn.m.r. spectrum also contained a low intensity signal at -4.19 p.p.m. which may be due to IF_4OMe. Its infrared spectrum (4000-400cm^{-1}, liquid film) contained peaks at 2951m, 2836w, 1449m, 1258w, 1148w, 973vs.br. 887s, 740w, 541 s br; 500 sh,cm^{-1}.

The decomposition of $IF_3(OMe)_2$ was followed by infrared spectroscopy over several days. The products were CH_2O, SiF_4, Me_2O and I_2.

(c) Preparation of $IF_2(OMe)_3$.

Trimethoxoiodine(V) difluoride, prepared from IF_5 (1.86g, 8.4.m. mol.) and $Me_2Si(OMe)_2$ (1.00g, 8.3 m. mol. followed by 0.50g, 4.2 m.mol. after 1½ h.) was characterised by its analysis (Found C, 13.2; H, 3.5; F, 14.3; I, 48.6%. $C_3H_9F_2IO_3$ requires C, 14.0; H, 3.5; F, 14.7; I, 49.2%), and by its n.m.r. and mass spectra. I.r. spectrum (4000-400, liquid film) 2940m, 2827m, 1443m, 1135sh, 975vs.br., 890w, 861w, 520v s.br, cm^{-1}

(d) Preparation of $IF(OMe)_4$

Tetramethoxoiodine(V) monofluoride, prepared from IF_5 (2.42g, 10.9m.mol.) and $Me_2Si(OMe)_2$ (1.13g, 10.9 m.mol. followed after ½ h. by the same amount), analysed as C, 16.3; H, 4.3; F, 8.2; I, 49.2% ($C_4H_{12}FIO_4$ requires C, 17.8; H, 4.4; F, 7.0; I, 47.0%). The sample may have contained Me_2SiF_2 as an impurity, indicated by its n.m.r. spectra.

Its decomposition at 20°C was observed over 2 weeks and the products were CH_2O, SiF_4, Me_2O and I_2. I.r. spectrum (4000-400cm^{-1}, liquid film) 2932m, 2818m, 1442m, 987s.br, 870w, 505s, cm^{-1}.

(e) Preparation of $I(OMe)_5$

Pentamethoxoiodine was prepared from IF_5 and an excess or stoicheiometric quantity of Me_3SiOMe or $Me_2Si(OMe)_2$. It was not isolated pure but contaminated with traces of $IF(OMe)_4$ or other alkoxo-fluorides. However,

purer products, according to the n.m.r. data, were obtained when near stoicheiometric quantities of $Me_2Si(OMe)_2$ were employed.

I.r. spectrum (4000-400cm^{-1}) 2935m, 2917m, 1975w.br., 1445m, 1150sh, 985vs.br, 865m, 500s.br, cm^{-1}.

$I(OMe)_5$ decomposes overnight to give I_2, CH_2O, Me_2O and other unidentified products. No reaction was detected between $I(OMe)_5$ and pinacol.

The Reactions of IF_5 with $Me_{4-n}Si(OEt)_n$.

(f) Preparation of IF_4OEt.

Ethoxoiodine(V) tetrafluoride was prepared from IF_5 and Me_3SiOEt or $Me_2Si(OEt)_2$. It is a colourless liquid and was characterised by its n.m.r. and mass spectra by comparison with IF_4OMe. It decomposed more rapidly than IF_4OMe.

I.r. spectrum (liquid film 4000 - 400cm^{-1}) 2990m, 2938w, 1474m, 1457sh, 1440m, 1397s, 1362w, 1148w, 1093m, 984vs, 876vs, 686m, 654m, 566vs.br, cm^{-1}.

(g) Preparation of $IF_3(OEt)_2$

Diethoxoiodine(V) trifluoride, prepared from IF_5 and $Me_2Si(OEt)_2$ was a colourless involatile liquid. It was characterised by its mass spectrum by comparison with $IF_3(OMe)_2$. Its ^{19}Fn.m.r. spectrum was a broad peak δ -13 p.p.m., width at $\frac{1}{2}$-height = 200Hz, and its proton n.m.r. spectrum (Table 4) showed the expected ethyl resonances. Its i.r. spectrum (4000-400cm^{-1}, liquid film) contained peaks at 2980s, 2938m, 2907sh, 1476s, 1446s, 1385s, 1360m, 1316w, 1248w, 1200m, 1151m, 1092s, 1000s.br, 880vs, 743m, 555vs.br, cm^{-1}. Among its decomposition products were diethyl ether and acetaldehyde.

(h) Preparation of $IF_3OMeOEt$.

Methoxo-ethoxoiodine(V) trifluoride, prepared from IF_4OMe and Me_3SiOEt in CH_3CN, was a colourless involatile liquid. Its ^{19}Fn.m.r. spectrum (Table 4) and mass spectrum (Table 5.6) suggested that it was a mixture.

I.r. spectrum (4000-400 m^{-1}, liquid film) 2982w, 2950w, 2902sh, 2836w, 1467sh, 1447m, 1386m, 1361w, 1257w, 1150w, 1091s, 989vs.br, 879vs.br, 754m, 545vs.br, 502sh, cm^{-1}.

Reaction of Iodine Pentafluoride with Trimethylphenoxosilane.

Excess IF_5 was added to Me_3SiOPh (0.16g, 9.8m.mol.) at -196°C. The reaction mixture was allowed to warm overnight to 20°C to produce a black solid and SiF_4 and Me_3SiF, identified by their i.r. spectra. The black solid was partially soluble in CH_3CN. Its ^{19}Fn.m.r. spectrum contained peaks at δ +5 (width at $\frac{1}{2}$-height = 90 Hz), and 112 p.p.m. Its ^{1}Hn.m.r. spectrum had a low intensity signal at δ 8.3 p.p.m. On hydrolysing the black solid HF was vigorously produced.

Reactions of Methoxoiodine(V) Tetrafluoride.

With Pyridine

IF_4OMe (2.27g, 10.3m.mol.) was soluble in excess pyridine at -50°C. After 15 mins. a white solid is precipitated from solution. After removal of pyridine a pale brown solid was isolated. It analysed as IF_4OMepy. Elemental analysis. Found C, 22.8; H, 2.6; F, 24.1; N, 4.3% $C_6H_8F_4INO$ requires: C, 23.0; H, 2.6; F, 24.3; N, 4.5% I.r. spectrum (4000-400cm^{-1} nujol mull.) 3139w, 3075w, 1959w, 15365, 1592m, 1492s, 1289s, 1218w, 1192s, 1168s, 1060m, 1032w, 963m, 896sh, 885s, 877s, 821w, 796w, 776s, 679vs, 610w, 500s.br, cm^{-1}.

The solid was sparingly soluble in CH_3CN and pyridine. No ^{19}Fn.m.r. signals were detected but the ^{1}Hn.m.r. spectrum contained signals at δ= 8.2, 8.0 and 7.6 attributable to pyridine and a signal at δ 3.9 p.p.m. (δ Me = 3.33 p.p.m. in $Me_4N^+I^-$).

With benzene

IF_4OMe was soluble in C_6H_6 below 0°C giving a colourless solution. The chemical shifts of IF_4OMe in benzene are presented in Table 3. The solution became pale brown after 1 day and SiF_4 was detected. The ^{19}Fn.m.r. spectrum after 3 days contained peaks at δ+18 p.p.m., doublet,

J = 96 Hz; -1.4 p.p.m.; -143 p.p.m.; -173 p.p.m. The ^{1}H n.m.r. spectrum containeda broad resonance centred at δ 3.9 p.p.m. (width at $\frac{1}{2}$ height = 48 Hz) and signals at δ 4.0, 3.0, 2.9 and 2.7 p.p.m. along with the benzene resonance at δ 3.1 p.p.m. A mass spectrum of the volatiles contained peaks due to C_6H_6, SiF_4 and low intensity peaks at $^{m}/_{e}$ 115 and 96 are assigned to $C_6H_4F_2^+$ and $C_6H_5F^+$ respectively.

With Arsenic Pentafluoride.

Excess AsF_5 was added to IF_4OMe(approximately 1.2g, 5.4 m.mol.) and the mixture allowed to warm slowly to room temperature from -80°C. giving a blue-green solution. Unreacted AsF_5 was removed at -80°C. A ^{1}Hn.m.r. of the remaining product, a blue green liquid, contained one signal at δ 5.0 p.p.m. and the ^{19}Fn.m.r. consisted of one strong signal at δ-23.4 p.p.m. which appeared to have sidebands δ-20.6 and -26.2 p.p.m. After 5 days the ^{1}Hn.m.r. spectrum contained peaks at δ 5.6, 5.1 and 4.5 p.p.m.

The room temperature volatiles were removed leaving a solid. Elemental analysis: As, 12.7; F, 34.2; I, 32.0% IF_4OMe. AsF_5 requires As, 23.9; F, 54.5; I, 40.4%. The solid decomposed to a sticky liquid after 1 day. I.r. spectrum of liquid (4000-400cm^{-1}) 3060m, 2980w, 1642m, 1443m, 1145w.br, 920m.br, 710s, 670m, 600m.br,cm^{-1}. The material, volatile at 20°C, was dissolved in CCl_3F to give a pale green solution. Its ^{19}Fn.m.r. spectrum contained a sharp singlet at δ7.2 p.p.m. and its ^{1}Hn.m.r. spectrum a singlet at δ1.9 p.p.m. The CCl_3F was removed to leave an orange crystalline solid. I.r. spectrum (1200-400cm^{-1}, nujol mull.) 1190w, 760m, 705s, cm.$^{-1}$.

Decomposition of IF_4OMe.

The decomposition of IF_4OMe at 20°C was followed by i.r. spectroscopy over 10 days. After 4 hours the sample went mushy. SiF_4 and I_2 were detected. After 2 days traces of another product were observed.

After 10 days significant amounts of this product were detectable. I.r. spectrum (4000-400cm^{-1} vapour phase) 2950w, 2930w, 1766m, 1756s, 1744m, 1218m, 1208s, 1189m, 1175m, 1167m, 1153m. The volatile products were removed leaving a brown white solid. I.r. spectrum (1300-400cm^{-1}, nujol mull.). 1073w, br, 1043w, 828s, 809s, 712s, 630s, 605sh, 493m,cm^{-1}.

The thermal decomposition of IF_4OMe, also followed by i.r. spectroscopy, produced a colourless liquid at 64°C, which gave off volatile products, identified as mainly CH_2O and SiF_4, at 85°C. At approximately 95°C, the sample decomposed instantaneously producing, in addition to the above products, HI, CO, possibly MeF and I_2.

II Reaction of Perfluoro-alkyl and aryl iodine(V) Tetrafluorides with Methylalkoxosilanes

The Reactions of CF_3IF_4 and $Me_{4-n}Si(OMe)_n$, (n = 1, 2)

are summarised in Table 6; Quantitative formation of Me_3SiF was observed in reaction 1, observed 0.27g, calculated 0.28g. The i.r. spectra of the individual products are presented here. (4000-400cm^{-1}).

1. CF_3IF_3OMe; (liquid film 2945m, 2837m, 1443m, 1296sh, 1254v s., 1064v.s, 1010w, 975sh, 965s, 950sh, 844m, 834m, 747s, 570s br, cm^{-1}.

2. $CF_3IF_2(OMe)_2$: (liquid film) 2985sh, 2945s, 2812s, 2292m, 1452sh, 1440s, 1217v.s, 1044w, 1062v.s, 972v.s, 837s, 746 v.s, 500 v s, br. cm^{-1}.

3. $CF_3IF(OMe)_3$: (nujol mull and liquid film) 2931w, 2812w, 1503s, 1277m, 1210s, 1177s, 1085s, 1006w, 977s, 960sh, 854sh, 815s, 740s, 547m, 520s, 503sh, 446s, cm^{-1}.

p The Reactions of $C_2F_5IF_4$ with $Me_2Si(OMe)_2$ trum could not be obtained.

The Reactions of $C_2F_5IF_4$ with $Me_2Si(OMe)_2$.

$Me_2Si(OMe)_2$ (0.99g, 8.3 m.mol.) was added to $C_2F_5IF_4$ (0.25g, 7.8 m.mol.) in CCl_3F and the mixture allowed to react at 20°C for 1 h. The ^{19}Fn.m.r. spectrum of the reaction mixture contained signals at δ -17, -31.2 p.p.m. and -78.3 p.p.m. and the ^{1}H.n.m.r. contained signals

at δ 4.54 and 4.01 p.p.m. Signals due to Me_3SiF_2 were also detected.

I.at δ 4.54 and 4.01 p.p.m. Signals due to Me_3SiF_2 were also detected.

12I.r. spectrum (4000-400cm^{-1}, liquid film) 2940m, 2932w, 1439m, 1308s,

Th1239s, 1191s, 1113s, 985s, 908s, 855sh, 742s, 632m, 597sh, 525s.br, cm^{-1}.

peThe mass spectrum contained peaks attributable to C_2F_5I and the following

m/peaks indicated the presence of a $R_FIF_{4-n}(OMe)_n$: (m/e 127 = 100)

18m/e = 215, (1.5) IF_3OMe^+; 196 (1.5), CF_3I^+, IF_2OMe^+; 195 (1) $IF_2OCH_2^+$;

31189 (2), $I(OMe)_2^+$; 181 (1), IOF_2^+; 158 (19), $CF I^+$, $IFOMe^+$; 157(7) $IOCH_2^+$;

Reaction of $(CF_3)_2CFIF_4$ with Me_3SiOMe.

$(CF_3)_2CFIF_4$(1.25g, 3.4 m.mol.) and Me_3SiOMe(0.31g, 3.0 m.mol.) in CCl_3F reacted at 20°C. Me_3SiF and a colourless liquid were produced.

Nm.r. data on reaction mixture indicated only the presence of Me_3SiF and decomposition products, $(CF_3)_2CFI$ being among them. Infrared spectrum (4000-400cm^{-1}, liquid film) 2950m, 2845w, 1446m, 1393w, 1371w, 1285s, 1237s, 1144m, 1117sh, 1068w, 1022w, 960s, 880s, 850s, 749s, 719sh, 712s, 689w, 560s.br, cm^{-1}.

The colourless liquid decomposed at 20°C, giving an unidentified yellow solid, $(CF_3)_2CFI$ and possibly CH_2O.

Reaction of $C_4F_9IF_4$ with Me_3SiOMe.

Varying stoicheiometries of reactants were employed. An involatile liquid was produced but decomposed within 1h and was not isolated.

Reaction of $C_6F_5IF_4$ with Me_3SiOMe.

$C_6F_5IF_4$ (0.48g, 1.3 m.mol.) and Me_3SiOMe (0.10g, 9.6m.mol.) in CCl_3F were allowed to react at 20°C for 30 mins. The products were a colourless liquid and Me_3SiF. The liquid decomposed after a few hours at room temperature to give an unidentified yellow solid.

The ^{19}Fn.m.r. spectrum contained signals δ -7.7 (triplet, $C_6F_5IF_4$), -21.0 (broad triplet), -39.8 and -40.7 (possibly a doublet), -116.6, -127.8 (broad), -144.9, -146.9 (possibly a doublet), -158.3(CH_3SiF), -160.7

(complicated signal), -163.6 (IF_3) p.p.m.

No signals, except those of Me_3SiF, were detected in the ^{1}Hn.m.r. spectrum. The ^{19}Fn.m.r. signals quickly disappeared on standing and were not further investigated. A low temperature study and decoupling experiments might aid assignments of the species present.

I.r. spectrum (4000-400 cm^{-1}, liquid film) 2930 w.br, 1633m, 1497m,br, 1400m, 1366w, 1345w, 1289m, 1259m, 1138sh, 1093s, 990s.br, 920w.br, 841s, 806sh, 797s, 759s, 718m, 691vw, 662vw, 617sh, 620sh, 562s.br, 484sh, cm^{-1}.

III The Reactions of Iodine Pentafluoride with some Organosilicon Compounds. Trimethylchlorosilane.

Several reactions were attempted. All produced similar results.

A mixture of IF_5(1.87g, 8.4 m.mol.) and Me_3SiCl (0.90g, 8.3 m.mol.) reacted smoothly at -45°C to form a yellow solid and Me_3SiF. The mass spectrum of the solid contained the following peaks:

m/e = 254 (100), I_2^+; 222(3), IF_5^+; 203(27), IF_4^+; 184(9), IF_3^+; 165(2), IF_2^+; 164(3), $I^{37}Cl^+$; 162(10), $I^{35}Cl^+$; 146(3), IF^+; 127(50), I^+; 74(3), $^{37}Cl_2^+$; 72(12), $[^{37}Cl\ ^{35}Cl]^+$; 70(16), $^{35}Cl_2^+$; 37(5), $^{37}Cl^+$; 35(12), $^{35}Cl.^+$

The solid was soluble in CH_3CN and pyridine. The ^{19}Fn.m.r. spectrum in CH_3CN showed a doublet at δ+5.4 p.p.m. and a quintet at δ+59.5 p.p.m. The ^{19}Fn.m.r. spectrum in pyridine contained a broad peak at δ+ 7.1 p.p.m, width at $\frac{1}{2}$ - height = 60 Hz. The solid decomposed rapidly at room temperature to IF_5, I_2, Cl_2 and probably ICl. Therefore it was not fully characterised. A pale yellow solid was isolated from pyridine solution. Elemental analysis: C, 25.1; H, 2.4; Cl, 7.2; F, 19.7, I, 39.8; N, 5.7%. Atomic ratios, C:H:Cl:F:I:N = 2.1: 2.4: 0.2:1.0: 0.3: 0.4. $C_5H_5ClF_4IN$ requires C, 18.9; H, 1.6; Cl, 11.2; F, 23.9; I, 40.0; N, 4.4%.

This solid was soluble in IF_5. Only one ^{19}Fn.m.r. signal was observed at δ+22.1 p.p.m. The infrared spectrum of this solid (4000-400cm^{-1}, nujol mull) comprised peaks at 3080sh, 1630w, 1606sh, 1602m, 1249w, 1218sh, 1210m, 1170sh, 1109sh, 1059s, 1040m, 1010s, 955sh, 880m, 759vs, 749s, 721sh, 686vs, 676sh, 650s, 634s, 577vs.br, 546s, 478vs,br, 440m, 428sh,cm^{-1}. Other peaks were obscured by nujol.

Hexamethylsiloxane

A mixture of IF_5(3.78g, 17.0m.mol.) and $(Me_3Si)_2O$ (1.30g, 8.0m.mol.) did not react at -80°C. The mixture was allowed to warm overnight to 20°C. SiF_4, Me_3SiF and possibly Me_2SiF_2 were detected by i.r. spectroscopy. I_2 and an involatile liquid were also produced. I.r. spectrum of involatile liquid (4000-400cm^{-1}) 2982w, 1450m, 961s, 880m, 689m, 601sh, 570s.br,cm^{-1}.

Trimethylpentafluorophenoxosilane.

IF_5(1.46g,6.6m.mol.) added to $Me_3SiOC_6F_5$(0.82g, 3.2 m.mol.) formed a reddish brown solution at 20°C. After 3 days,traces of Me_3SiF were detected by i.r. spectroscopy. The ^{19}Fn.m.r. only contained signals due to IF_5 and $Me_3SiOC_6F_5$ but in the ^{1}Hn.m.r. spectrum there were low intensity signals at δ 3.65, 4.11, 4.80 p.p.m.

$Me_3SiOCH(CF_3)_2$ and $Me_3SiOC(CF_3)_2OCH(CF_3)_2$

IF_5(0.91g,4.1 m.mol.) and a mixture of approximately 2:1 $Me_3SiOCH(CF_3)_2$ and $Me_3SiOC(CF_3)_2OCH(CF_3)_2$ (0.29g) gave a colourless reaction mixture at 20°C. The mixture was then heated to 40-50°C for 2 hours and left at 20°C for 3 days. Me_3SiF was not detected. A sample of the reaction mixture showed signals in the ^{19}Fn.m.r. spectrum attributable to $Me_3SiOCH(CF_3)_2$ and $Me_3SiOC(CF_3)_2OCH(CF_3)_2$ and broad signals at δ+ 11.2 (width at half-ht. = 120 Hz) and +57.4 p.p.m. A low intensity signal at δ-4.8 p.p.m. was also present. The ^{1}Hn.m.r. spectrum contained signals due to starting material and a low intensity

signal at δ 3.40 p.p.m. After 13 days, the ^{19}Fn.m.r. spectrum showed new low intensity signals at δ-76.3, -133.3 (multiplets) and -153.2 p.p.m. The latter two signals may be due to Me_2SiF_2 and Me_3SiF.

Methyltrimethylsilylsulphide.

A mixture of IF_5(2.01g, 9.1 m.mol.) and Me_3SiSMe (1.07g, 9.0 m.mol.) were allowed to warm slowly to -50°C. No reaction occurred. Between -50°C and room temperature, an exothermic reaction occurred producing I_2, Me_3SiF and HF among other products. An infrared spectrum of the volatiles at 20°C indicated the presence of SOF_2. A mass spectrum of the volatiles displayed peaks at $^{m}/_{e}$ 96, $Me_2SiF_2^+$; 92, Me_3SiF^+; 89, SF_3^+; 86, SF_2O^+; and fragment ions of these species. The ^{19}Fn.m.r. spectrum contained two signals at δ-159, multiplet (Me_3SiF), and -164, singlet, (IF_3) p.p.m. The ^{1}Hn.m.r. spectrum confirmed the presence of Me_3SiF. A doublet at δ+10 p.p.m., assigned to IF_5 disappeared after several days and the peak at δ-164 p.p.m. increased in intensity.

Diethylaminotrimethylsilane.

IF_5(1.91g, 8.6 m.mol.) was added to $Me_3SiN(Et)_2$ (1.25g, 8.6 m.mol.) at -196°C. The mixture was allowed to warm slowly by careful control of a -196°C bath. As the liquids warmed slightly, a vigorous reaction took place. On recooling the mixture detonated.

IV The Reactions of Iodine Pentafluoride with Trimethylsilyl Acetates.

These reactions were performed in cooperation with Mr. O.R. Chambers during his B.Sc. thesis[168].

Trimethylsilyl Trifluoroacetate(a) A mixture of IF_5(1.47g, 6.6 m.mol.) and $Me_3SiOC(O)CF_3$(0.62g, 3.3 m.mol.) was deep red at 20°C. The flask became warm and after 10 mins the reaction mixture was colourless. An infrared spectrum of the volatiles at -30°C indicated Me_3SiF and/or Me_2SiF_2. After another hour the mixture again became warm and a black solid was deposited. The liquid layer was purple. An i.r. spectrum

of the volatiles at -80°C indicated Me_3SiF[165] and Me_2SiF_2[166]. Several bands at 690, 1100, 1200-1280 and 1900cm^{-1} were also observed. The spectrum of the room temperature volatiles contained a significant extra peak at 1815cm^{-1}. The peaks at 1900 and 1815cm^{-1} are tentatively assigned to the carbonyl stretching frequencies of $CF_3C(O)F$ and $MeOC(O)CF_3$ respectively (literature values 1901 and 1802 for $EtOC(O)CF_3$[167].) A mass spectrum of the volatiles contained peaks at $^{m}/_{e}$ 128, $CF_3CO_2Me^+$; 116, $CF_3C(O)F^+$; 99, CF_3CO^+; 109, $CF_2CO_2Me^+$; 96, $Me_2SiF_2^+$; 69, CF_3^+; 57, CO_2Me^+; The ^{19}Fn.m.r. spectrum showed signals at δ+56.3 (quintet) and +9.2(doublet, J=100Hz) assigned to IF_5; δ -78 (may be doublet J = 1Hz), -135 p.p.m. (multiplet) assigned to Me_2SiF_2. Low intensity signals at -60, -78.1 and -15 7 p.p.m. (assigned to Me_3SiF) were also observed. The ^{1}Hn.m.r. spectrum contained signals attributable to Me_2SiF_2 and Me_3SiF, a singlet at δ 3.7 p.p.m. and a low intensity singlet at δ 4.3 p.p.m.

(b) The experiment was repeated with IF_5 (1.80g, 8.1 m.mol.) and $Me_3SiOC(O)CF_3$(0.56g, 3.0 m.mol.) with similar results. Analysis indicated that the black solid contained ca. 80% iodine.[169]

Trimethylsilyl Acetate.

(a) A rapid reaction occurred between IF_5(0.93g, 4.5 m.mol.) and $Me_3SiOC(O)CH_3$(0.44g, 3.3 m.mol.) at the melting point of IF_5, 10°C, to give a black solid (I_2) and a purple liquid. The liquid was a mixture containing Me_2SiF_2, Me_3SiF and $CH_3C(O)F$ (C=O stretch 1872cm^{-1})[167] assigned on their i.r. and mass spectra. A ^{1}Hn.m.r. spectrum of the reaction mixture in CCl_3F confirmed the presence of Me_3SiF and Me_2SiF_2 and two singlets at δ 3.4 and 1.7 p.p.m. are assigned to methyl acetate (literature values δ 3.65 and 2.01 p.p.m.)[80]. A black solid (I_2) and traces of an unidentified viscous liquid remained on removing the volatile material.

(b) IF_5(1.96g, 8.8 m.mol.) and $Me_3SiOC(O)CH_3$ (1.04, 7.8 m.mol.) reacted

as before. The volatile products, identified by their i.r. and mass spectra, were Me_2SiF_2, Me_3SiF and $CH_3C(O)F$. A ^{1}Hn.m.r. spectrum of the reaction mixture indicated that the ratio Me_2SiF_2: Me_3SiF was less than in (a). Signals ascribed to MeOC(O)Me were also detected but the spectrum contained several other peaks which could not readily be assigned. The signals appeared at δ 4.4 p.p.m. (low intensity), 4.2 and 3.5 p.p.m. (of equal intensity), 2.0, 1.9 and 1.8 p.p.m. A ^{19}Fn.m.r spectrum of the volatile products in CCl_3F contained signals at δ-136 and -162 p.p.m. assigned to Me_2SiF_2 and Me_3SiF and an intense signal at δ-168 p.p.m. The ^{1}Hn.m.r. spectrum contained signals due to $CH_3OC(O)CH_3$. A black solid (I_2) and a viscous liquid were isolated from the reaction mixture. An i.r. spectrum of the liquid contained many broad peaks consistent with C-H, C=O and I-F or I-O bonds. Infrared spectrum (4000-400cm^{-1} liquid film) 2950 w.br, 1700 s.br, 1588 s, 1512m, 1420sh, 1385s, 1353sh, 1260mbr, 1230m.br, 1071m, 1036m, 907s, 823sh, 767sh, 679m, 600s, 510s, cm^{-1}.

The mass spectrum contained the following peaks (Relative intensities are included in ref. 168) $^m/_e$ 254, I_2^+; 233, $IF_4OCH_2^+$; 222, IF_5^+; 215, $IF_3OCH_3^+$; 203, IF_4^+; 184, IF_3^+; 181, IF_2O^+; 165, IF_2^+; 146, IF^+; 127, I^+; 90, $C_3H_6O_3^+$; 74, $C_3H_6O_2^+$; 62, $C_2H_3FO^+$; 59, $C_2H_3O_2^+$; 43, $C_2H_3O^+$; indicating the presence of IF_5, IF_4OMe, MeC(O)F and MeC(O)OMe.

V Reactions of Fluoromethylsilanes with IF_5

Tetramethylsilane.

IF_5(1.14g, 5.2 m.mol.) and Me_4Si(0.54g, 6.1 m.mol.) formed a colourless mixture at 20°C. The reaction was followed by n.m.r. and i.r. and mass spectrometry. After approximately 36h, Me_3SiF was detected by i.r. spectroscopy and a ^{19}Fn.m.r. contained signals due to IF_5 and and Me_3SiF. Other signals at δ-4.9 and -167 p.p.m. were tentatively assigned to CH_3IF_4 and IF_3 respectively. The ^{1}Hn.m.r. spectrum showed

a doublet due to Me_3SiF and two singlets δ 2.01, unassigned and 4.32 p.p.m., which may be due to CH_3IF_4. Significant quantities of Me_2SiF_2 were detected by mass spectrometry after another 2 days ($^m/_e$ = 96, $Me_2SiF_2^+$). A small peak at $^m/_e$ = 100 was detected in the mass spectrum of the volatiles after 6 days. SiF_4 was detected throughout the reaction. On mixing IF_5(1.40g, 6.3 m.mol.) and Me_3SiF (0.67g, 7.3 m.mol.) at 20°C, iodine and HF were produced. The mixture was distilled onto NaF to remove HF. The ^{19}Fn.m.r. spectrum of the reaction mixture after 7 days indicated that approximately one quarter of the Me_3SiF had been converted to Me_2SiF_2. The spectrum also contained signals due to IF_5 and a small peak at δ 5.4 p.p.m.(CH_3IF_4). The ^{1}Hn.m.r. spectrum confirmed the presence of Me_3SiF and Me_2SiF_2. It also contained a complicated signal at δ 0.61 p.p.m. and a low intensity singlet at δ 4.16 p.p.m. The mass spectrum contained ions at $^m/_e$ = 96 and 81 assigned to $Me_2SiF_2^+$ and $MeSiF_2^+$ but no ion at $^m/_e$ = 100 ($MeSiF_3$).

The reaction was repeated in an attempt to isolate CH_3IF_4, using IF_5 (1.31g, 5.8 m.mol.) and Me_3SiF (0.57g, 6.2 m.mol.) but HF and I_2 were produced and no species was isolated.

Dimethyldifluorosilane

IF_5(1.63g, 7.4 m.mol.) and Me_2SiF_2(0.71g, 7.5 m.mol.) form a pale pink solution which turns brown at 20°C over 3 days. After 20 days at 20°C a low intensity signal 4 p.p.m. downfield from the signal due to Me_2SiF_2, was observed in the ^{19}Fn.m.r. spectrum of the reaction mixture. Increasing amounts of SiF_4 were also detected over the 20 day period.

Reaction of Methoxoiodine(V) tetrafluoride and Trimethylfluorosilane.

IF_4OMe (1.26g, 5.4 m.mol.) and Me_3SiF (0.56g, 6.1 m.mol.) were mixed at 20°C. Over 4 days SiF_4 was produced but no Me_2SiF_2 was detected.

VI Reactions of Iodine Pentafluoride with Sulphite Esters.
Dimethyl sulphite.

(i) IF_5 (~9g, 40 m.mol.) dissolved in $(MeO)_2SO$ (~4g, 36 m.mol.) at -20°C to give a pale pink solution, the n.m.r. spectrum of which, after several hours at 20°C, displayed resonances due to IF_5, MeOS(O)F (δ_{Me} = 3.901 p.p.m δ_F = +53.8 p.p.m., J_{HF} = 1Hz). The i.r. and mass spectra of the reaction volatiles confirmed the identification of MeOS(O)F[132]. Singlets in the ^1H and ^{19}Fn.m.r. spectra at δ 4.8 p.p.m. and δ-5.2 p.p.m. respectively are assigned to IF_4OMe. On removing the volatiles at 20°C a white solid was observed but not isolated.

(ii) IF_5 (1.14g, 5.1 m.mol.) and $(MeO)_2SO$ (0.76g, 6.9 m.mol.) formed a pale pink solution at 20°C. The ^1Hn.m.r. spectrum of the reaction mixture contained signals at δ 3.66, 3.89 and 4.47 p.p.m. attributable to $(MeO)_2SO$, MeOS(O)F and IF_4OMe respectively. The ^{19}Fn.m.r. spectrum contained signals at δ-8 and +54.8 p.p.m. attributable to IF_4OMe and MeOS(O)F and resonances due to IF_5. After several hours at 20°C the ^1Hn.m.r. spectrum indicated that the amount of IF_4OMe and MeOS(O)F had increased relative to $(MeO)_2SO$. After another period of several hours the ratio of IF_4OMe : MeOS(O)F: $(MeO)_2SO$ was approximately 1:1:1. IF_5 could still be detected. A sample of liquid involatile at -30°C was isolated.

Elemental analysis found C, 8.1; H, 2.0; F, 26.7; I, 44.2; S, 5.4%
$2IF_4OMe.(MeO)_2SO$ requiies C, 8.1; H, 2.1; F, 26.3; I, 43.9; S, 5.5%
I.r. spectrum: (4000-400cm^{-1}) 3008w, 2950m, 2832w, 1452s, 1228sh, 1191s, 960vs, 892w, 740sh, 710s, 600-400cm^{-1}, broad absorption. On addition of pyridine to the mixture, an exothermic reaction occurred and a white solid was isolated.

Elemental analysis: Found C, 17.1; H, 2.7; F, 33.3; I, 41.5; N, 32; S, 0.8%. I.r. spectrum (4000-400, nujol and fluorolube mulls.), 3139w,

3098m, 3088m, 1633m, 1587w, 1490s, 1289s, 1191s, 1167w, 1133w, 1060m, 1050sh, 1040w, 1029w, 1010m, 961w, 882s, 876s, 776s, 737m, 680s, 651w, 638w, 587s, 470s.br, cm^{-1}.

Diethyl sulphite.

A mixture of IF_5(3.39g, 16.0 m.mol.) and $(EtO)_2SO$ (0.96g, 7.0 m.mol.) was allowed to warm to room temperature from -196°C. An exothermic reaction occurred and the reaction mixture became pink. Three methylene resonances were observed in the ^{1}Hn.m.r. spectrum at δ 4.52 p.p.m., J = 7Hz, $(EtO)_2SO$; δ 4.36 p.p.m., J = 8Hz, $EtOS(O)F$; δ 4.90, J = 9Hz, IF_4OEt. The methyl signals overlapped and were less easily assigned. The ^{19}Fn.m.r. spectrum contained signals at δ+ 57.9, $EtOS(O)F$ and δ-3.3 p.p.m., IF_4OEt. An ill-resolved doublet due to IF_5 was also observed. An involatile liquid was isolated from the reaction mixture. Infrared spectrum: (1300 - 400cm^{-1}, liquid film) 1245sh, 1230s, 1215sh, 1187sh, 1084w, 990m, 921m, 888m, 783w, 680w, 600-500vs.br.cm^{-1}.

Diphenyl sulphite.

A mixture of IF_5(0.98g, 4.4 m.mol.) and $(PhO)_2SO$ (0.79g, 3.6 m.mol.) which contained traces of PhOH reacted slowly at -20°C and violently at room temperature. The volatile products were identified as SO_2 and SiF_4 by their i.r. spectrum. The other products were iodine and tar.

VII Reactions of Iodine Pentafluoride with Trimethyl Phosphite.

(i) A violent reaction occurred between IF_5(1.44g, 6.5 m.mol.) and $P(OMe)_3$(0.92g, 7.4 m.mol.) at -35°C and purple fumes were observed. The fraction volatile at -80°C was mainly methyl fluoride with traces of methyl iodide and dimethyl ether. A ^{19}Fn.m.r. spectrum of the remaining brown liquid contained signals at δ-9.1 p.p.m. (width at half-ht = 60 Hz), -69.4 p.p.m., J = 710 Hz and δ-86.2 p.p.m., J = 976 Hz. These resonances were assigned to IF_4OMe, PF_6^- and $(MeO)_2P(O)F$ respectively. The ^{1}Hn.m.r. spectrum displayed a broad envelope of

TABLE 12

^{1}H and ^{19}F n.m.r. data of some fluorophosphorus compounds

Compound	$-\delta_F$ (p.p.m.)	J_{P-F} (Hz)	δ_H (p.p.m.)	J_{P-H} (Hz)	Ref.
$(MeO)_3PF_2$	72.8	706	3.65	15	170
$(MeO)_2P(O)F$	86.9	970			170
MeOP(O)(F)Me	62	1039	3.81(OMe)	11	157
			1.65(Me)	19	
$(MeO)_3P^+Me.PF_6^-$	73	707	4.3(OMe)	11	157
			2.4(Me)	18	
Unknown	62.9	732	3.60	15	125
$(MeO)_2P(O)Me$			3.66(OMe)	11	171
			1.43(Me)	17	
$P(OMe)_3$			3.72	11	172
$PF(OMe)_2$	63.1	1208	3.59	10	157
IF_4OMe	9.0		4.33		

TABLE 13

^{1}H and ^{19}F chemical shifts and assignments of some products from $IF_5/P(OMe)_3$ reaction.

Assignment	Reaction	$-\delta_F$ (p.p.m.)	J_{P-F} (Hz)	δ_H (p.p.m.)	J_{P-H} (Hz.)
$(MeO)_3PF_2$	(ii)	71.5	721		
$(MeO)_2P(O)F$	(i)	86.2	976		
	(ii)	85.3	981		
$(MeO)_3^+PMe\ PF_6$	(i)	69.4	710	2.00(Me)	11
Unknown	(ii)	61.5	727	3.44	14
$(MeO)_2P(O)Me$	(ii)			1.31(Me)	18

peaks in the region δ 3.8 to 4.4 p.p.m. consistent with the presence of P-OMe or I-OMe groups. A low intensity doublet at δ 2.0 p.p.m. J = 14Hz was characteristic of a P-Me group.

The liquid product decomposed at 80°C to an unidentified white solid. CH_2O, SiF_4 and Me_2O were also detected. The solid was soluble in C_6F_6. A low intensity signal, at δ -129 p.p.m., was detected in the ^{19}Fn.m.r. spectrum and in the ^{1}Hn.m.r. spectrum two low intensity peaks at δ 5.0 and 4.2 p.p.m. Two doublets, J = 12Hz, resonated at δ 3.46 and δ 3.41 p.p.m.

(ii) $P(OMe)_3$ (0.94g, 7.5 m.mol.) and IF_5 (0.43g, 1.9 m.mol.) were allowed to react at -78°C. A vigorous reaction, which was controlled by alternate -196°C and -78°C cold baths, occurred but no purple fumes were observed. Only MeF was detected and removed at -78°C. MeI was detected at 20°C. After several hours at 20°C, the reaction mixture produced MeF and Me_2O. A ^{19}Fn.m.r. spectrum of the reaction mixture comprised doublets at δ_A -61.5 p.p.m., J = 727 Hz; δ_B - 71.5 p.p.m., J = 721 Hz and δ_C - 85.3, J = 981 Hz. δ_B is tentatively assigned to $(MeO)_3PF_2$ and δ_C to $(MeO)_2P(O)F$. The ^{1}Hn.m.r. spectrum contained signals at δ 4.06, 3.89, 3.81, 3.62, 3.42, 3.35, 3.17, 3.13, 3.04, 2.22, 1.99, 1.73, 1.34, 1.03 p.p.m. After several hours at 20°C the spectra became somewhat simplified. The main differences were that the doublet at δ -61.5 p.p.m. in the ^{19}F spectrum disappeared as well as a singlet at δ 3.35 p.p.m. and a shoulder on the signal at δ 3.61 p.p.m. The spectrum then contained a number of signals attributable to POMe groups. It was thought that this region contained three doublets δ 3.50 p.p.m, J = 12Hz; δ 3.83 p.p.m, J = 11Hz; δ 3.64 p.p.m., J = 11Hz. Two doublets, attributable to P-Me, at δ 2.20p.p.m., J = 18Hz and δ 1.31 p.p.m., J = 17Hz and singlets at 3.19 p.p.m., assigned to Me_2O and δ 1.11 p.p.m.

TABLE 14

Mass spectral data for reaction (ii)

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
140	3		80	16	CH_2OPF^+
128	5	$C_2H_6O_3P^+F$	79	12	$CH_4O_2P^+$ PO_3^+
127	3	$C_2H_5O_2P^+F$	78	3	$CH_3O_2P^+$
124	< 1	$C_3H_9O_3P^+$	77	1	$CH_2O_2P^+$
113	1	$CH_3O_3PF^+$	69	3	PF_2^+
112	3	$C_2H_6O_2P^+F$	68	8	
111	2	$C_2H_5O_2P^+F$	67	29	$HPOF^+$
110	16	$C_2H_4O_2P^+F$	66	37	POF^+
109	8	$C_2H_6O_3P^+$	65	3	CH_3PF^+
103	1	$C_2H_7O_2PF^+$ $CH_3O_3PF^+$	64	1	CH_2PF^+
101	1	O_2P $CH_4OPF_2^+$	63	4	O_2P^+
100	1	$CH_3OPF_2^+$	62	1	$C_2H_6O_2P^+$
99	1	$CH_2OPF_2^+$			
98	100	$CH_4O_2PF^+$ PO_3F^+	51	1	HPF^+
97	37	CH_3O_2PF	50	1	PF^+
95	6	$CH_4O_3P^+$ PO_4^+			
93	2	$C_2H_6O_2P^+$	48	13	HPO^+
85	2	POF_2^+	47	24	PO^+
82	2	CH_4POF^+ PO_2F^+	45 31	7 37	CH_2P^+ P^+ CH_3O^+
81	40	CH_3POF^+	30	8	CH_2O^+
			29	32	CHO^+

Metastable Transitions

m_1	Transition	m_2	m^* obsd.	m^* cald.
	unassigned		86.4	
	unassigned		77.7	
128	$C_2H_6O_3PF^+ \quad CH_4O_2PF^+ + CH_2O$	98	75.0	75.0
98	$CH_4O_2PF \quad CH_2OPF^+ + H_2O$	80	65.3	65.3
112	$C_2H_6O_2PF^+ \quad CH_4OPF^+ + CH_2O$	82	60.0	60.0
	unassigned		58.2	
	unassigned		57.3	
82	$CH_4OPF \quad HOPF^+ + CH_3$	67	54.7	54.7

assigned to CH_3I were also observed.

The mass spectrum of the room temperature volatiles is listed in Table 14

A liquid film i.r. spectrum of the reaction mixture was recorded: ($4000-400cm^{-1}$) 3000sh, 2962s, 2862s, 1463s, 1427sh, 1379sh, 1313s, 1280s, 1188s, 1040s, 911s, 845s, 820sh, 788m, 770w, 753m, 736m, 714sh, 563sh, 523sh, 503s, 484sh, 489s.

Reaction of Methoxoiodine(V) Tetrafluoride with Trimethyl Phosphite.

$P(OMe)_3$(0.56g, 4.5 m.mol.) was added to IF_4OMe(0.98g, 4.2 m.mol.), and the reaction allowed to warm to 20°C overnight. Separation of the most volatile products yielded Me_2O, and traces of MeI. The remaining products were an involatile liquid and traces of a brown solid, both of which were dissolved in CH_3CN. The ^{19}Fn.m.r. spectrum contained a singlet at δ -9.8 p.p.m., presumably due to IF_4OMe, and a doublet at -73.3, J = 722 Hz attributable to PF_6^-. The proton n.m.r. contained a singlet at δ 4.09p.p.m. due to IF_4OMe and a doublet at δ 3.64 p.p.m., assigned to $P(OMe)_3$. Low intensity signals were observed at δ 4.16 and 3.97 p.p.m. and even smaller signals were detected, implying that the mixture contained trace quantities of other compounds.

CHAPTER THREE

FLUORINE-18 EXCHANGE BETWEEN TRIMETHYLFLUOROSILANE AND SUBSTITUTED DERIVATIVES OF TUNGSTEN HEXAFLUORIDE

INTRODUCTION

Up to 1934, the use of radioactive techniques was confined to a small number of naturally occurring radioactive isotopes such as bismuth and lead, but the discovery of artificial radioisotopes, especially of the lighter elements, opened up a much wider field of study. The successful operation of nuclear reactors and the continued development of particle accelerators has made available radioisotopes, both short- and long-lived, of nearly all the elements. This coupled with the production of reliable and sensitive detection equipment has caused the early exploratory and qualitative work to be superceded by quantitative and more detailed investigations.

Much of the earlier qualitative work was designed to obtain information on the nature and strength of bonds, on the assumption that an ionic bond will interchange groups or atoms more readily than a covalent bond and that for a series of bonds of similar type, the weakest bond will interchange most readily.[174] These concepts have been employed in the study of isotopic exchange reactions. Because exchange reactions occur at equilibrium with respect to chemical species involved, although not with respect to the distribution of isotopes among the various chemical species, these reactions are particularly useful for the investigation of reaction kinetics and mechanisms.

Despite the wide use of fluorine in nuclear energy work, the use of fluorine radioactive isotopes has not been greatly exploited in studying chemical reactions and physical changes. Fluorine, as found in nature, is monoisotopic, ^{19}F. The known radioactive isotopes of fluorine, all man-made, are ^{17}F, ^{18}F and ^{20}F. However, only ^{18}F is sufficiently long-lived to serve as a tracer (half-life = 110 mins). This nuclide was first described by Snell[176] as a product of the bombardment of neon gas with 5 MeV

deuterons and by Pool, Lark and Thornton from the reaction $^{19}F(n, 2n)^{18}F$.[175] It has since been shown that ^{18}F can be produced by a wide variety of nuclear reactions[177] but only a few of these methods yield a product of high radiochemical purity and relatively high specific activity. The choice of preparation method and target materials depends on the type of machine available and the subsequent treatment of the sample for extraction of ^{18}F. The most useful method of obtaining carrier free ^{18}F is from the sequence of reactions, $^{6}Li(n, \alpha)t$; $^{16}O(t, n)^{18}F$.[178] The nuclide ^{18}F emits an 0.65 MeV positron which is usually detected by its associated gamma ray.

In spite of the practical difficulties involved in handling the short-lived ^{18}F isotope and the reactive nature of many fluorine compounds, a number of ^{18}F exchange systems have been investigated and these may be separated into three main types (a) reactions with elemental fluorine, (b) reactions with HF and (c) reactions of other fluorine compounds.

Systems involving elemental fluorine are noteworthy for the absence of free radical mechanisms in view of the low dissociation energy of fluorine and the significant concentrations of fluorine atoms at temperatures exceeding 150°C. In general, exchangesinvolving elemental fluorine have been studied by labelling the other component rather than the element itself, although F_2 may be labelled directly. Dodgen and Libby[179] appear to have been the first investigators to use ^{18}F in chemical exchange studies. They were concerned with halogen exchange in the gas phase between hydrogen halides and the corresponding halogen. Unlike the systems HCl/Cl_2, HBr/Br_2 and HI/I_2, HF and F_2 gases do not undergo exchange at room temperature. Heating to 200°C for about an hour in a brass vessel was necessary to accomplish exchange. It was demonstrated and later confirmed by Adams and his co-workers[180] that the observed exchange is heterogeneous, catalysed by metal fluoride on the wall of the vessel. Dodgen and Libby concluded that unlike HX and X_2 (X = Cl, Br, I), HF and

F_2 does not form an intermediate of the type HX_3, due to a lack of higher electron orbitals in the fluorine atom or, if the complex is formed, the position of the hydrogen atom in the complex prevents exchange.

Surface catalysed processes also operate in the exchange reactions between the halogen fluorides and fluorine although competing homogeneous processes have been inferred for ClF_3 and IF_7, where the following dissociation reactions :

$$ClF_3 \rightleftharpoons ClF + F_2 \qquad 1.$$

$$IF_7 \rightleftharpoons IF_5 + F_2 \qquad 2.$$

seem plausible in view of the low dissociation energies involved. Although ClF_5 is known, it is unlikely that concentrations of this molecule, kinetically significant enough to compete with the dissociative process (equation 1) would be produced in the low pressure systems employed in these exchange studies. In contrast to ClF_3 and IF_7, no homogeneous contribution to fluorine exchange is expected for BrF_5 since BrF_5 is known to be undissociated up to 400°C. However, Adams, Bernstein and Katz[181] have shown that the BrF_5/F_2 system has a homogeneous component at higher concentrations of BrF_5. The experimental data are consistent with a bimolecular associative process.

Sheft and Hyman[182] have examined the exchange reactions of the hexafluorides of sulphur, xenon, molybdenum, tungsten, osmium, iridium and uranium with fluorine in the gas phase. The least reactive fluoride is SF_6, which did not exchange at temperatures up to 350°C. The most reactive is XeF_6 for which rates of exchange at 100°C and 150°C have been measured. The rate is a linear function of the fluorine concentration so that the reaction, if homogeneous, appears to have an associative mechanism. UF_6 and OsF_6 also exchange with fluorine by an associative

mechanism but IrF_6 does not show a dependence on the fluorine concentration and the mechanism is thought to be dissociative. The other work on the hexafluorides has not been published in full, but tungsten and molybdenum hexafluorideshave been reported to undergo rapid exchange with fluorine.

Gas phase exchanges between $H^{18}F$ and the halogen fluorides ClF_3, BrF_3, BrF_5 and IF_7 have been studied at 27°C by Rogers and Katz.[183] These exchanges are essentially complete within the time of reaction and separation (3 min) and, as identical results are obtained both in a copper and in a Kel-F vessel, the mechanism is more likely to be homogeneous than heterogeneous. In view of the absence of evidence for an atomic mechanism in the F_2-ClF_3 system, the mechanism of exchange in this case is thought to involve the formation of intermediate complexes of the type $HF.ClF_3$ or $HF.IF_7$. Similar combinations of HF and halogen fluoride have also been examined in solution along with the HF-IF_5 and HF-SbF_5 systems. All show complete exchange within ten minutes. In view of the high dielectric constant and,in several cases,the high electrical conductivities of these mixtures, associative and/or ionic mechanisms are likely. It is noteworthy that in these systems no differences have been detected between the rates of exchange of structurally different fluorine atoms in the same molecule. No exchange is observed between HF and SF_6[183] or fluoromethanes.[184] Since sulphur and carbon are completely saturated in these compounds, the complexes $HF{\cdot}CF_nH_{4-n}$ and $HF{\cdot}SF_6$ would be expected to have large activation energies and, hence, slow exchange rates.

The heterogeneous systems, HF with CuF_2, ZnF_2 or AlF_3 show signs of exchange[179,183] and a mixture of $H^{18}F$ and NaF shows complete exchange within 3 minutes.[183] In addition to their intrinsic interest, metal fluorides and metal hydrogen difluorides have been used to produce ^{18}F labelled volatile fluorides. The alkali metal salts are the most reactive.[185]

Recently, fluorine exchange has been studied between $\overset{*}{CsF}$ and BrF_5 (* denotes labelled atom). The exchange is though to proceed via donor-acceptor complex of the type $CsBr\overset{*}{F}_6$ according to the scheme.[186]

$$\overset{*}{CsF} + 2BrF_5 \longrightarrow CsBr\overset{*}{F}_6 + BrF_5$$

$$CsBr\overset{*}{F}_6 + BrF_5 \rightleftharpoons CsBrF_6 + \overset{*}{BrF}_5$$

Similarly, exchange in the NaF, UF_6 system occurs via Na_2UF_8.[187]

Isotopically labelled BF_3, SiF_4, PF_5, POF_3, AsF_5, SF_4, SOF_2 and SeF_4 have been prepared by their passage over heated $Li^{18}F$.[188] Exchange is suggested to occur via the formation of a short-lived intermediate between LiF and the covalent fluoride; for example, for SF_4 the intermediate may be formulated as $LiSF_5$. Unlike the HF, fluoromethane systems, the alkali metal fluorides have been found to exchange readily with fluorocarbons. The metal fluoride exchanges more readily with C_3F_6 than with CF_4, C_4F_{10} and $(C_2F_5)_2O$ although appreciable exchange is observed in all cases.[189] The reactive fluoromethylene group of C_3F_6 has been already discussed in Chapter I. Recently, in a detailed study ^{18}F exchange has been observed between the Group I fluorides (Cs-Li inclusive) and trifluoroacetyl fluoride or sulphur tetrafluoride at 150 and 50°C.[190] In agreement with Gens and his co-workers[189] the order of exchange observed is :

$$Cs > Rb > K > Na > Li$$

The results have been interpreted in terms of the formation of the anions $C_2F_5O^-$ and SF_5^-.

$Cs^{18}F$ has been used by Majid[191] to prepare labelled trimethylfluorosilane. $Me_3\overset{*}{SiF}$ has, in turn, been employed in the study of exchange reactions between $Me_3\overset{*}{SiF}$ and substituted derivatives of tungsten hexafluoride. Substituted derivatives of WF_6 and covalent fluorides, in general, can be prepared by reaction of the binary fluoride with organosilanes, Me_3SiX

(for example, X = Cl, OR or NR_2). The exchange reactions were investigated in an attempt to shed some light on the mechanism of substitution. It was found that ^{18}F exchange for WF_5OMe , $WF_4(OMe)_2$ and WF_5NEt_2 is fast and nearly complete after 180 minutes. The rate of exchange for WF_5OPh and $WF_5OC_6F_5$ is slow but easily detected and the rate of exchange for $WF_2(NEt_2)_4$ is intermediate, whereas no exchange is observed between Me_3Si^*F and $WF_2(OMe)_4$ even after 180 minutes. The exchange between WF_6 and Me_3SiF was not investigated as complete separation of the components of the mixture was not possible.

In the present work, it was intended to apply this technique to investigate substitution reactions of iodine (V) fluorides. However, a quantitative investigation of the kinetics of tungsten fluorides, WF_5X, was desirable prior to the application of the technique to the thermally less stable iodine fluorides. WF_5OMe and WF_5OPh were chosen because of their stability at room temperature, their ease of preparation, and their solubility in C_6F_6. Unfortunately, due to the difficulties encountered in this section of the work, there was not enough time available to investigate the iodine fluoride systems. However, the additional knowledge gained will be of use in undertaking a study of ^{18}F exchange with I-F compounds.

RESULTS AND DISCUSSION

Discussion of Results

The results of exchange reactions between Me_3Si^*F and inactive WF_5OMe and WF_5OPh are given in Tables 1-8. The reactions were carried out at 26 ± 1°C in homogeneous systems in which Me_3Si^*F was added to a solution of WF_5X (X = OMe or OPh) in hexafluorobenzene. Majid[191] observed no exchange, up to 50°C, between inactive C_6F_6 and Me_3Si^*F, Cs^*F or labelled WF_5OMe. The mole ratio of reactants used in this study was 1:1 for WF_5OMe:Me_3SiF and WF_5OPh:Me_3SiF. The WF_5OPh system was also studied using a four-fold excess of trimethylfluorosilane.

The fraction of ^{18}F exchanged (f) is calculated from the expression :[181]

$$f = \frac{A_1}{A_1 + A_2} \Big/ \frac{n_1 m_1}{n_1 m_1 + n_2 m_2} \qquad 1.$$

where A = activity (counts s^{-1}) after exchange, corrected for decay m(mmol) = quantity of a species, WF_5X or Me_3SiF, with n exchangeable fluorine atoms, and subscripts 1 and 2 refer to the initially inactive and active species respectively. In this case 1 refers to the tungsten compound and 2 to Me_3Si^*F. Errors in f due to weighings are estimated to be negligible compared with those from count rate determinations. The error quoted is the relative error in f, and is determined from the equation :[192]

$$\frac{\sigma_f}{f} = \frac{1}{A_1 t} + \frac{1}{(A_1 + A_2)t'} \qquad 2.$$

where A_1 and A_2 are as in equation 1 above, and t and t' are the counting times for compounds 1 and 2 respectively. In the present work $t = t' = 40$ s.

The calculation of the fraction exchange, f, is based on the assumption that all the fluoride ligands of the tungsten compounds are exchangeable; that is $n_1 = 5$.

However, the five fluorines may not be exchangeable at the same rate. It may be that the fluorine atom *trans* to the OR group is exchanged at a significantly different rate from the four fluorines *cis* to OR. This effect, if present, should be seen in a graph of log $(\frac{1}{1-f})$ vs t. Two other possibilities exist : 1) that only fluorine *trans* to OR is exchangeable ($n_1 = 1$) and, 2) that only the fluorines *cis* to OR are exchanged ($n_1 = 4$). Majid noted that when $n_1 = 1$, unreasonable values of f are obtained for WF_5NEt_2 and WF_5OMe, so that this possibility is excluded. The fraction exchange calculated $n_1 = 4$ or 5 for WF_5OMe and WF_5NEt_2 are not significantly different and as the exchange does not appear to be complete after the longest time of observation, the value of n_1 cannot be unambiguously determined in the present work.

It is general practice to reject data in which the radiochemical balance is $< 95\%$, but in the present work the f values have been recalculated, f_R, on the theoretical total activity. In most cases it is found that this calculation lessens the spread of results.

The rate of exchange of fluorine, at a particular temperature in reaction :

$$WF_5X + Me_3Si^{*}F \longrightarrow W^{*}F_5X + Me_3SiF$$

may be expressed in terms of the concentration of reactants in dynamic equilibrium at time t, by a modified form of McKay's equation :[193]

$$R = \frac{2.303}{t} \frac{nab}{na + b} \log \frac{1}{1-f} \qquad 3.$$

where R is the rate of exchange in $mol.Kg^{-1}min^{-1}$, t is the time of exchange in minutes, a is the molality of the tungsten compound with n equivalent exchangeable fluorines (n = 5 in this case), b is the molarity of Me_3SiF and f is the fraction exchange, as defined by expression 1.

Plots have been made of $\log (\frac{1}{1-f})$ vt (Figs. 1-8) for the exchange reactions of WF_5X with $Me_3\overset{*}{S}iF$. The rate of exchange R is then given by :

$$R = 2.303 \frac{nab}{na + b} \times \text{slope}$$

As stock solutions WF_5X were used the value of a in each plot is constant, but b varies from sample to sample and an average value of b is used to calculate R, b_{av}.

The rate of exchange for WF_5OMe has been calculated from Table 1 and Fig. 1 to be 1.45×10^{-3} $mol.Kg^{-1}min^{-1}$. The plot of $\log (\frac{1}{1-f})$ vt for WF_5OMe is a straight line passing through the origin, within experimental error. This suggests equal or almost equal rates of exchange for the two types of fluorine. As this data is based on only one experiment, small differences in the rate of exchange of fluorine trans to OMe and fluorine cis to OMe cannot be completely excluded.

The data in Fig. 2 and Table 2 refer to an impure sample obtained from the reaction between WF_6 and Me_3SiOMe. Instead of isolating WF_5OMe as a white solid as in the $WF_6/(MeO)_2SO$ reactions, the product was "mushy". The rate of exchange calculated for this sample is 2.37×10^{-3} $mol.Kg^{-1}min^{-1}$, which is faster than the rate for pure WF_5OMe. The plot of $\log (\frac{1}{1-f})$ vt does not pass through the origin suggesting that

Table 1

Exchange between Me_3SiF and WF_5OMe mole ratio ~1:1

WF_5OMe mmol	Me_3SiF mmol	A_2 counts s^{-1}	A_1 counts s^{-1}	$A_1 + A_2$ counts s^{-1} found	$A_1 + A_2$ counts s^{-1} theoretical	% error in counts	f	$\log \frac{1}{1-f}$	Time min.
0.669	0.665	1161	56	1217	1187	2.5	0.046 ± 0.036	0.020	35
0.598	0.647	964	67	1031	1038	0.3	0.079 ± 0.019	0.036	58
0.536	0.608	717	69	786	796	1.3	0.108 ± 0.020	0.050	90
0.654	0.710	645	115	760	767	0.9	0.184 ± 0.016	0.08[illegible]	125
0.525	0.608	478	114	592	594	0.3	0.237 ± 0.016	0.1[illegible]	151
0.574	0.654	467	107	574	550	4.4	0.229 ± 0.017	0.1[illegible]	182
0.670	0.637	284	114	398	411	3.2	0.341 ± 0.017	0.1[illegible]	257

Molality of WF_5OMe, a = 1.01,

molality of Me_3SiF, b_{av} = 1.26

Rate = 1.45×10^{-3} $mol.Kg^{-1}min^{-1}$

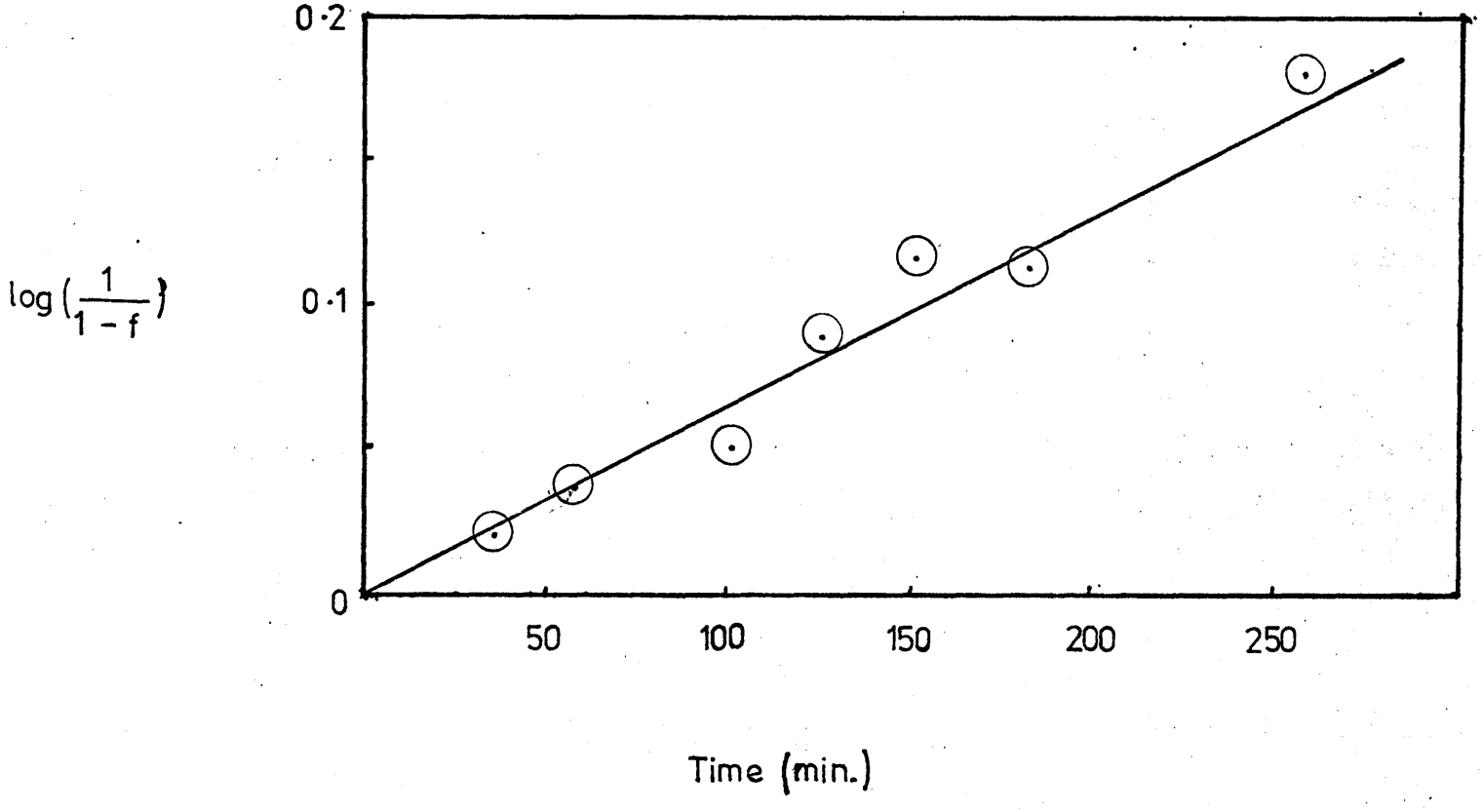


Fig. 1.

Table 2

Exchange between Me_3SiF and WF_5OMe mole ratio ~1:1

WF_5OMe mmol	Me_3SiF mmol	A_2 counts s^{-1}	A_1 counts s^{-1}	$A_1 + A_2$ counts s^{-1} found	$A_1 + A_2$ counts s^{-1} theoretical	% error in counts	f	$\log \frac{1}{1-f}$	Time min.
0.686	0.750	289	100	389	368	5.7	0.313 ± 0.018	0.163	30
0.693	0.728	192	101	293	298	1.7	0.417 ± 0.018	0.235	63
0.726	0.700	166	87	253	253	0.0	0.410 ± 0.020	0.239	90
0.522	0.721	139	91	230	235	2.1	0.504 ± 0.020	0.305	120
0.693	0.634	105	96	201	173	4.1	0.565 ± 0.020	0.362	151
0.562	0.847	96	93	189	180	5.0	0.640 ± 0.020	0.444	181

Molality of WF_5OMe, a = 1.03

molality of Me_3SiF, b_{av} = 1.18

$R = 2.37 \times 10^{-3}$ mol.$Kg^{-1}$$min^{-1}$

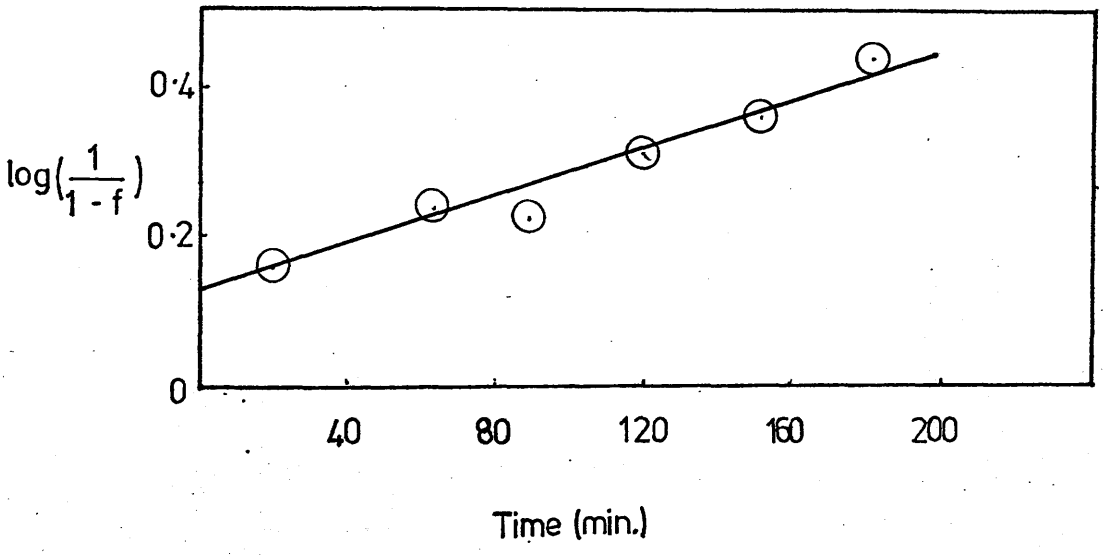

0·4
0·2
0
log(1/(1-f))
40
80
120
160
200
Time (min.)

Fig.2.

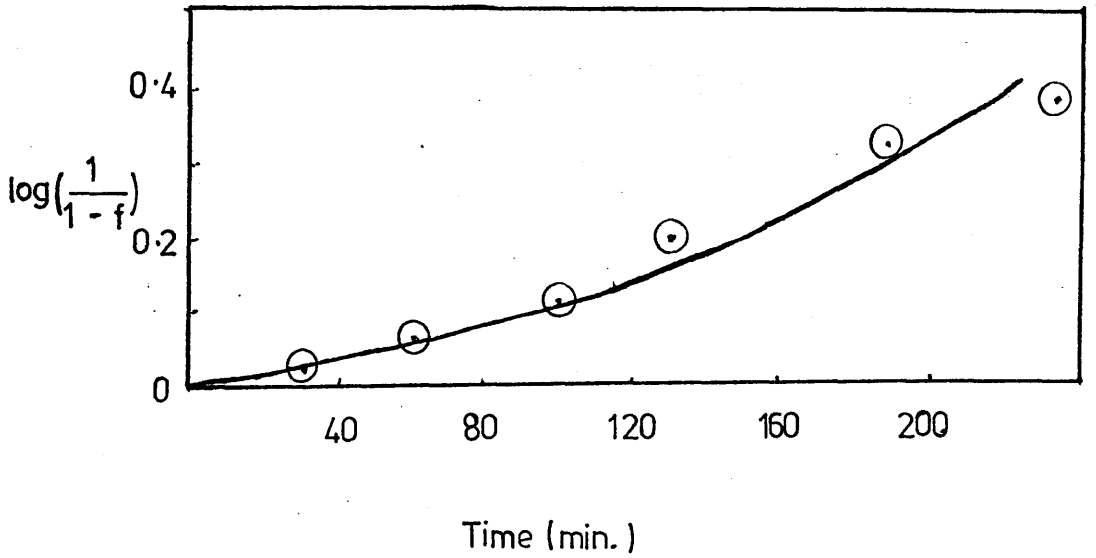

0·4
0·2
0
log(1/(1-f))
40
80
120
160
200
Time (min.)

Fig.3.

Table 3

Exchange between Me_3SiF and WF_5OMe mole ratio ~ 1:1

WF_5OMe mmol	Me_3SiF mmol	A_2 counts s^{-1}	A_1 counts s^{-1}	$A_1 + A_2$ counts s^{-1} found	$A_1 + A_2$ counts s^{-1} theoretical	% error in counts	f	$\log \frac{1}{1-f}$	Time min.
0.760	0.723	13080	759	13854	14060	1.4	0.065 ± 0.006	0.029	31
0.676	0.748	10770	1355	12125	12440	1.7	0.137 ± 0.004	0.064	61
0.660	0.741	7771	1764	9535	9417	1.3	0.227 ± 0.004	0.112	100
0.738	0.765	6479	2634	9113	8956	1.8	0.349 ± 0.503	0.186	125
0.717	0.686	5626	4443	10070	9423	5.8	0.526 ± 0.003	0.324	174
0.664	0.775	3875	3461	7336	7333	0.4	0.580 ± 0.003	0.377	233

Molality of WF_5OMe, a = 1.04,

molality of Me_3SiF, b_{av} = 1.10

Rate increase with time due to hydrolysis of sample

a fast initial exchange is occurring.

The data in Table 3 and Fig. 3 refer to a sample of WF_5OMe prepared from WF_6 and $(MeO)_2SO$. In the course of the exchange hydrolysis occurred and this may explain the increase in the rate of exchange with time.

Tables 4-6 list the data for the exchanges of WF_5OPh with $Me_3\overset{*}{S}iF$. When a radiochemical balance of 95% was not achieved, two values of the fraction exchanged are shown f and f_R. The rates from the data in Table 4 are $\underline{1.20 \times 10^{-3}\ mol.Kg^{-1}min^{-1}}$ from the uncorrected values and $\underline{1.03 \times 10^{-3}\ mol.Kg^{-1}min^{-1}}$ from the recalculated values, (Figs. 4a and b). At the end of both plots the rate appears to increase but this is probably due to the excess of $Me_3\overset{*}{S}iF$ used in this particular sample. The data in Table 5 are composed from two experiments. The figures from Table 5A are combined with the recalculated f values of Table 5B to give a rate of $\underline{1.02 \times 10^{-3}\ mol.Kg^{-1}min^{-1}}$. However, the validity of using theoretical activity values in calculating f must be in question as the rates from the two sets of f values in Table 6 give exchange rates of $\underline{1.08 \times 10^{-3}\ mol.Kg^{-1}min^{-1}}$ and $\underline{0.44 \times 10^{-3}\ mol.Kg^{-1}min^{-1}}$ from the uncorrected and corrected f values respectively. In experiment 6, WF_5OPh is in slight excess in most of the samples and this may cause a reduction in the exchange rate. The plots of $\log(\frac{1}{1-f})$ $\underline{vt}$ are straight lines which do not pass through the origin.

Tables 7 and 8 contain the data for exchange reactions of WF_5OPh with approximately a four-fold excess of $Me_3\overset{*}{S}iF$. Fig. 8 is a plot of $\log(\frac{1}{1-f_R})$ $\underline{vt}$ using corrected f values. The rate of exchange from Fig. 7 is $\underline{1.93 \times 10^{-3}\ mol.Kg^{-1}min^{-1}}$ and the rate from Fig. 8 is $\underline{1.64 \times 10^{-3}\ mol.Kg^{-1}min^{-1}}$. The intercepts on the $\log(\frac{1}{1-f})$ sides are 0.033 and 0.034 respectively. As expected, the rate of exchange increases

Table 4

Exchange between Me_3SiF and WF_5OPh ~ mole ratio 1:1

WF_5OPh mmol	Me_3SiF mmol	A_2 counts s^{-1}	A_1 counts s^{-1}	$A_1 + A_2$ counts s^{-1} found	$A_1 + A_2$ counts s^{-1} theoretical	% error in counts	f	$\log \frac{1}{1-f}$	Time min.	$\log \frac{1}{1-f_R}$	f_R
0.872	0.877	590	32	622	678	8.3	0.062 ± 0.029	0.027	35	0.025	0.057
0.572	0.689	429	44	473	490	3.5	0.115 ± 0.025	0.053	65		
0.740	0.860	409	49	458	485	5.6	0.132 ± 0.024	0.062	91	0.058	0.125
0.816	0.740	338	50	388	407	4.7	0.152 ± 0.024	0.072	124		
0.612	0.703	236	44	280	307	8.8	0.193 ± 0.026	0.093	153	0.084	0.176
0.671	1.180	335	81	416	448	7.1	0.263 ± 0.020	0.133	180	0.122	0.244

Molality of WF_5OPh, a = 1.35,

molality of Me_3SiF, b_{av} = 1.16

Rate $R = 1.20 \times 10^{-3}$ mol.Kg^{-1} min^{-1}

$R_R = 1.03 \times 10^{-3}$ mol.Kg^{-1} min^{-1}

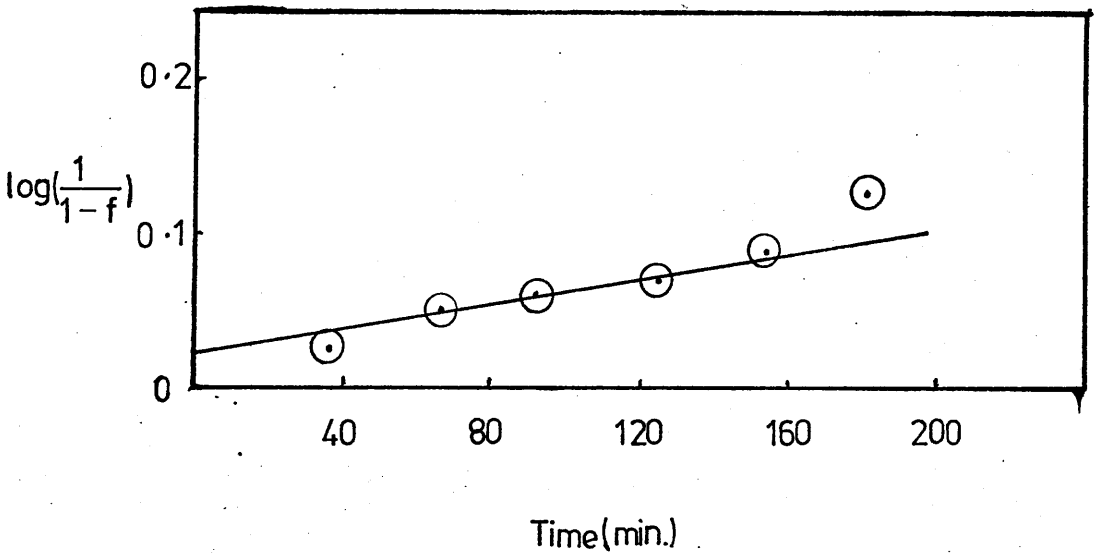

0·2
0·1
0
log(1/1-f)
40
80
120
160
200
Time(min.)

Fig. 4a.

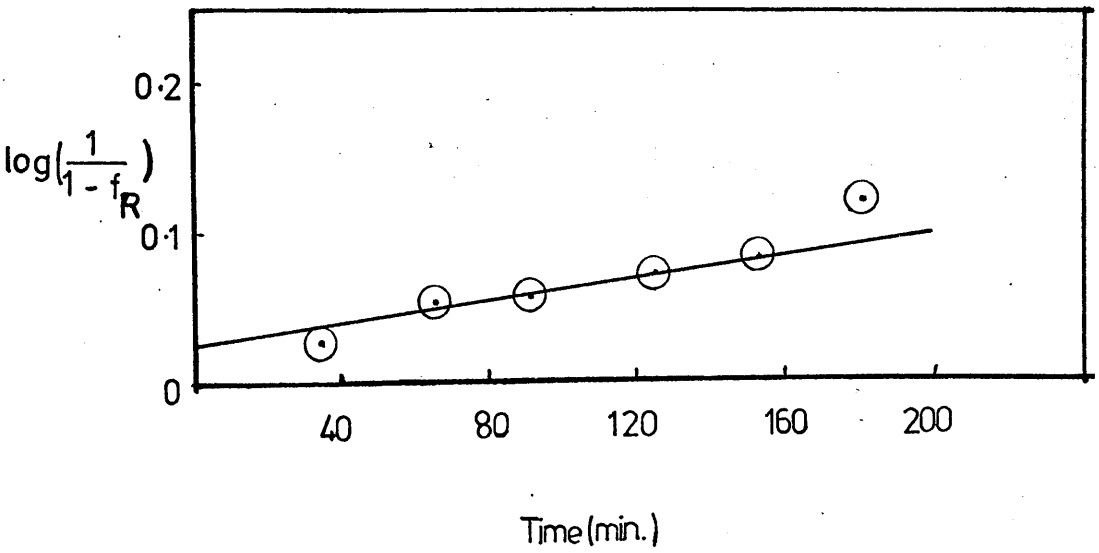

0·2
0·1
0
log(1/1-f_R)
40
80
120
160
200
Time(min.)

Fig. 4b.

Table 5

Exchange between Me_3SiF and WF_5OPh mole ratio ~1:1

A.

WF_5OPh mmol	Me_3SiF mmol	A_2 counts s^{-1}	A_1 counts s^{-1}	$A_1 + A_2$ counts s^{-1} found	$A_1 + A_2$ counts s^{-1} theoretical	% error in counts	f	$\log \frac{1}{1-f}$	Time min	$\log \frac{1}{1-f_R}$	f_R
0.531	0.508	14180	825	15005	15210	0.1	0.065 ± 0.006	0.029	35		
0.403	0.611	11095	1180	12275	12370	0.7	0.120 ± 0.005	0.057	70		
0.444	0.505	7247	931	8178	8254	0.9	0.140 ± 0.005	0.064	112		

molality of WF_5OPh, a = 0.80 molality of Me_3SiF, b = 0.90

B.

0.601	0.713	995	173	1168	1366	14.5	0.183 ± 0.013	0.088	94	0.074	0.157
0.584	0.674	831	154	985	1166	15.5	0.192 ± 0.014	0.093	120	0.077	0.163
0.655	0.674	684	162	751	975	22.7	0.200 ± 0.014	0.131	156	0.097	0.200
0.637	0.837	696	262	958	1095	12.5	0.345 ± 0.011	0.184	183	0.156	0.302

Molality of WF_5OPh, a = 1.11,

Molality of Me_3SiF, b_{av} = 1.27 Rate = R_R = 1.02×10^{-3} mol.Kg^{-1} min^{-1}

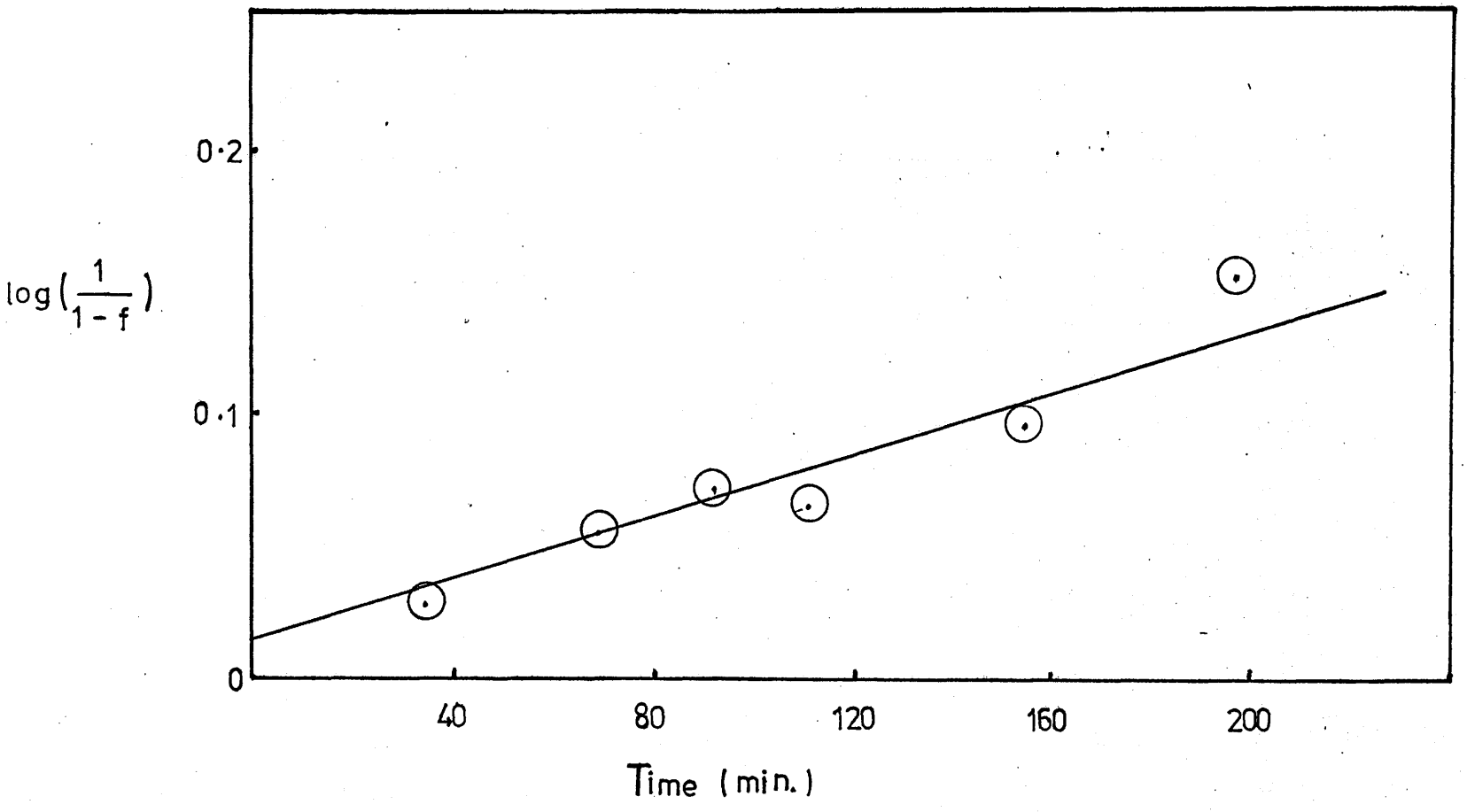


Fig. 5.

Table 6

Exchange between Me_3SiF and WF_5OPh mole ratio ~ 1:1

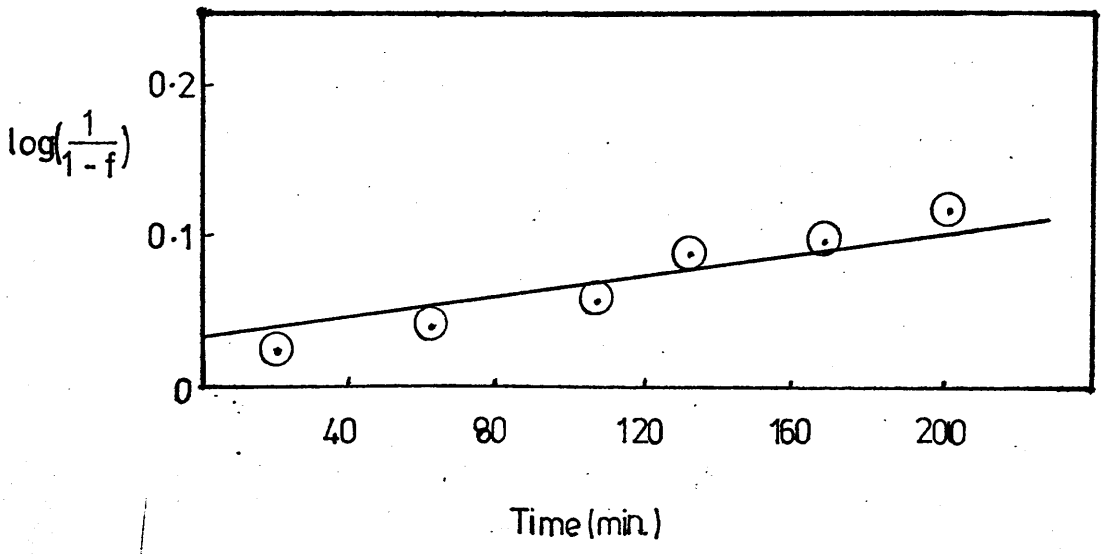
WF_5OPh mmol	Me_3SiF mmol	A_2 counts s^{-1}	A_1 counts s^{-1}	$A_2 + A_1$ counts s^{-1} found	$A_2 + A_1$ counts s^{-1} theoretical	% error in counts	f	$\log \frac{1}{1-f}$	Time min.	$\log \frac{1}{1-f_R}$	f_R
0.670	0.616	132	6	138	152	9.2	0.052 ± 0.066	0.023	72	0.021	0.047
0.686	0.634	97	8	105	141	25.1	0.090 ± 0.057	0.041	68	0.030	0.067
0.680	0.596	77	9	86	126	31.0	0.123 ± 0.055	0.057	97	0.030	0.084
0.605	0.620	61	11	72	120	40.0	0.184 ± 0.051	0.089	132	0.051	0.111
0.656	0.586	43	9	52	96	45.8	0.204 ± 0.057	0.099	168	0.051	0.111
0.705	0.599	34	9	43	86	50.0	0.244 ± 0.058	0.122	201	0.057	0.122

Molality of WF_5OPh, a = 1.12,

Molality of Me_3SiF, b_{av} = 1.02

Rate $R = 1.08 \times 10^{-3}$ mol. $Kg^{-1}min^{-1}$

$R_R = 0.041 \times 10^{-3}$ mol.$Kg^{-1}min^{-1}$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0·1
0
40
80
120
160
200
Time (min.)

Fig. 6a.

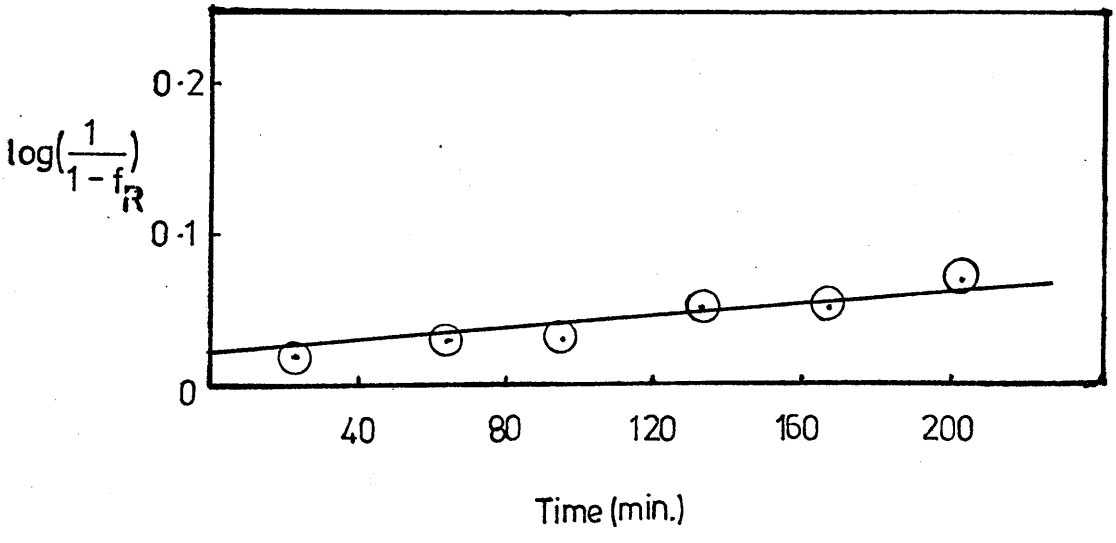

log(1/(1-f_R))
0·2
0·1
0
40
80
120
160
200
Time (min.)

Fig. 6b.

Table 7

Exchange between Me_3SiF and WF_5OPh mole ratio ~ 4:1

WF_5OPh mmol	Me_3SiF mmol	A_2 counts s^{-1}	A_1 counts s^{-1}	$A_1 + A_2$ counts s^{-1} found	$A_1 + A_2$ counts s^{-1} theoretical	% error in counts	f	$\log \frac{1}{1-f}$	Time min.
0.819	2.634	890	54	944	975	3.2	0.094 ± 0.022	0.043	34
0.628	2.708	788	52	840	844	0.5	0.115 ± 0.023	0.053	64
0.757	2.777	677	53	730	742	1.6	0.126 ± 0.022	0.058	92
0.708	2.704	549	48	597	623	4.2	0.142 ± 0.024	0.066	123
0.711	2.662	466	49	515	526	1.7	0.166 ± 0.024	0.079	154
0.734	2.742	432	49	481	489	1.6	0.178 ± 0.024	0.085	182

Molality of WF_5OPh, a = 1.35,

molality of Me_3SiF, b_{av} = 5.0704

Rate = 1.93×10^{-3} mol.$Kg^{-1}min^{-1}$

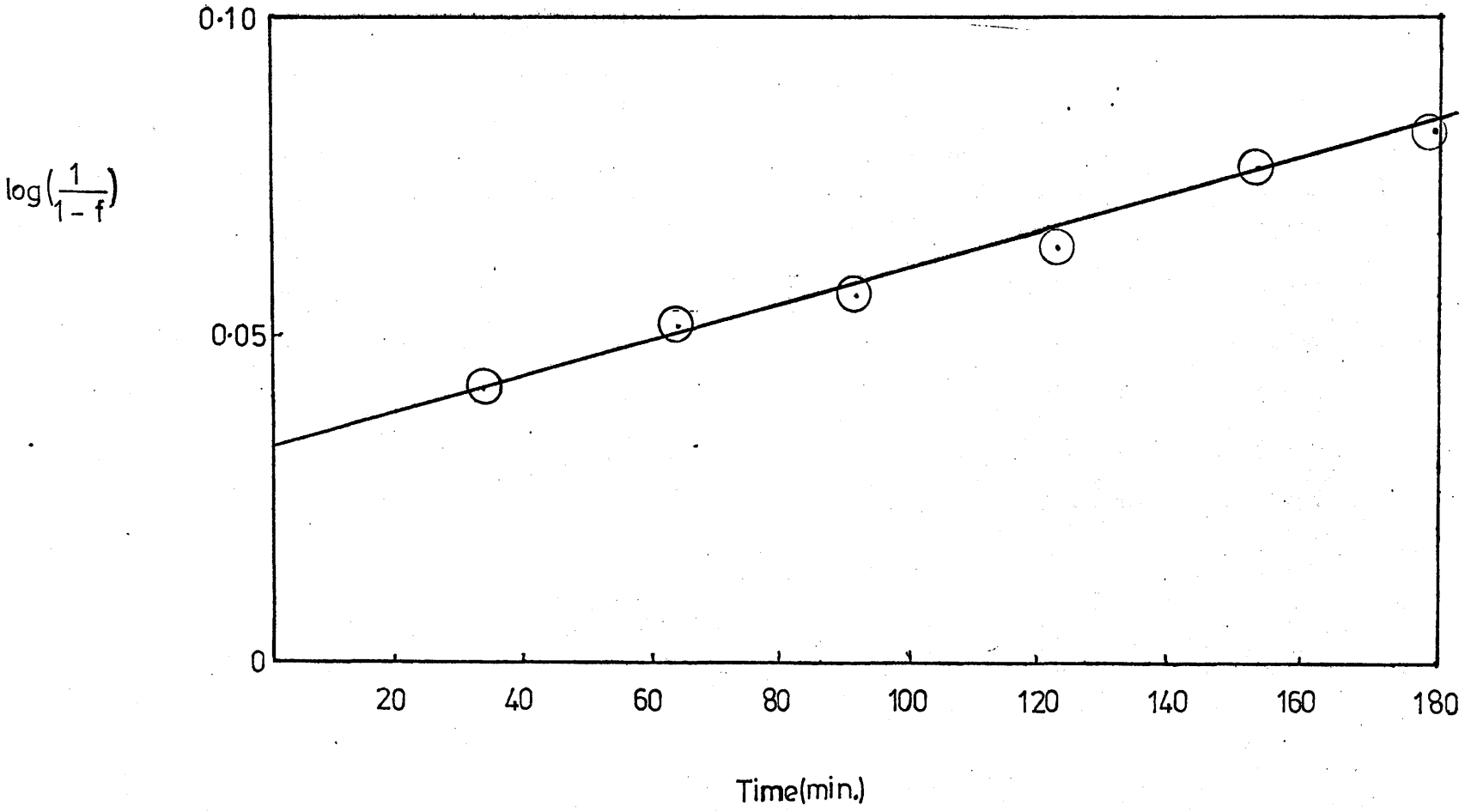

0·10
0·05
0
$\log\left(\frac{1}{1-f}\right)$
20
40
60
80
100
120
140
160
180
Time(min.)

Fig. 7.

Table 8

Exchange between Me_3SiF and WF_5OPh — mole ratio ~ 4:1

WF_5OPh mmol	Me_3SiF mmol	A_2 counts s^{-1}	A_1 counts s^{-1}	$A_1 + A_2$ counts s^{-1} found	$A_1 + A_2$ counts s^{-1} theoretical	% error in counts	f	$\log \frac{1}{1-f}$	Time min.	$\log \frac{1}{1-f_R}$	f_R
0.744	2.527	444	33	477	521	8.4	0.116 ± 0.028	0.049	32	0.049	0.106
0.622	2.442	354	29	383	482	20.5	0.135 ± 0.030	0.032	69	0.049	0.107
0.754	2.449	274	33	307	431	28.8	0.117 ± 0.029	0.085	101	0.580	0.126
0.573	2.419	234	41	275	410	32.9	0.275 ± 0.026	0.140	135	0.088	0.184
0.712	2.452	185	33	218	361	39.6	0.256 ± 0.030	0.128	171	0.073	0.154
0.649	2.512	147	40	187	329	43.2	0.380 ± 0.028	0.207	202	0.106	0.216

Molality of WF_5OPh, a = 1.12,

molality of Me_3SiF, b_{av} = 4.13

$R_R = 1.64 \times 10^{-3}$ mol.$Kg^{-1}min^{-1}$

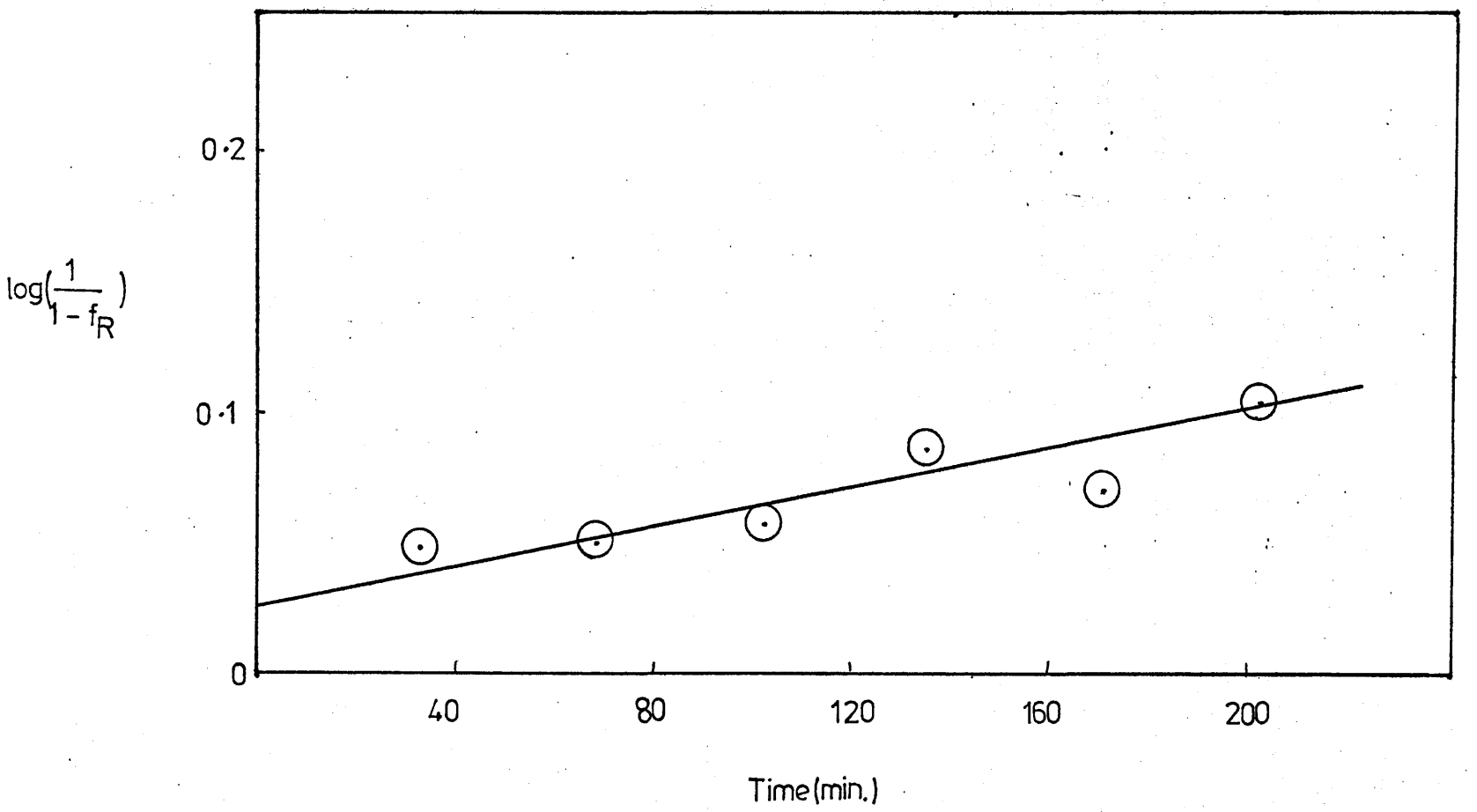


Fig. 8

as the amount of $Me_3\overset{*}{S}iF$.

The exchange rates for 1:1 mole ratios of WF_5X:Me_3SiF may be compared qualitatively. It appears that Me_3SiF and WF_5OMe exchange fluorines at a faster rate than Me_3SiF and WF_5OPh. However, a very fast initial exchange in the WF_5OPh, Me_3SiF system is not apparent in WF_5OMe, Me_3SiF. This fast initial exchange may be due to traces of HF arising from reaction of WF_6 with PhOH impurities in the Me_3SiOPh. It is noteworthy that when WF_5OMe is prepared from Me_3SiOMe, an impure product is obtained and the plot $\log(\frac{1}{1-f})$ vt also has a positive intercept.

Errors in f and hence in R due to count rate determinations and from loss of radioactivity have been discussed. Another source of uncertainty arises from variations in the composition of reaction mixtures. It has been shown in the $WF_5OPh/Me_3\overset{*}{S}iF$ system that the rate of exchange depends on the relative amount of $Me_3\overset{*}{S}iF$. By taking average values of b it is assumed that the variation of rate with $[Me_3\overset{*}{S}iF]$ is linear but this may not be the case.

Substitution at WF_6 by Me_3SiX is believed to involve a seven coordinate intermediate of the type :

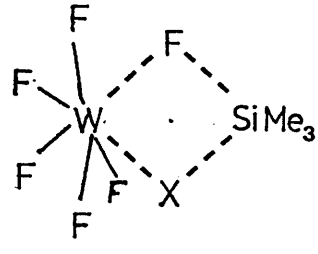


Fig. 9.

The formation of seven coordinate Lewis acid-Lewis base tungsten complexes has been reported and ^{19}F n.m.r. spectroscopic equivalence of fluorine atoms has been observed for the molecular complex

$WF_6 \cdot P(CH_3)_3$.[196] Assuming that ^{18}F exchange proceeds along a similar pathway, it is reasonable to suppose that all five fluorines may be equivalent in the transition state; that is $n_1 = 5$.

Discussion of Technique

The preparation of reactants and the technique involved in making up and counting the samples is described in the experimental section. On several occasions significant exchange between active $\overset{*}{CsF}$ and inactive Me_3SiF was not obtained. No reasonable explanation can be proposed for this as a similar routine was followed for each exchange and the purity of the reactants checked. If high ^{18}F activities in $Me_3\overset{*}{SiF}$ are not achieved, the observation of exchanges between $Me_3\overset{*}{SiF}$ and WF_5OR is impractical due to the short half-life of ^{18}F and the large errors inherent in a low count rate. Data based on count rates of < 25 counts s^{-1} should be discounted, although count rates below this have been included in Tables 1-8.

It is common practice in studying the kinetics of reactions of the type :

$$A + B \longrightarrow C + D$$

to have one reactant in large excess. This simplifies the kinetics, generally making the reaction pseudo- first order. In exchange systems discussed here it also has other advantages. Firstly, a large amount of fluorosilane gives a high count rate thus reducing the error in the calculated fraction exchanged. It would also allow the exchanges to be followed for a longer time, and it may, then, be possible to achieve equilibrium in the system and demonstrate that all the fluorines are exchangeable. One source of error in calculating absolute values for the rate of exchange is the deviation of reactants

from the 1:1 or 1:4 mole ratio in the individual experiments. By usingalarge excess of Me_3SiF deviations from the required stoicheiometry become negligible.

The amount of Me_3SiF used in any reaction can be controlled fairly accurately by careful control of the pressure but the amount of WF_5X, C_6F_6 is not as easy to control. The counting tubes were calibrated by measuring approximately 1 cm. from the bottom of the tube. However, the thickness of the base of the tube varies slightly from tube to tube producing a variation in the amount of solution in each sample. For studying exchanges of 1:1, 1:2, 2:1 etc. stoicheiometries, individual calibration of each tube might produce more accurate values of fraction and rate of exchange. The biggest source of error in the fraction exchanged arises from the low count rate in WF_5X after exchange. Using more WF_5X, either by increasing its concentration in C_6F_6 or by increasing the volume of solution used may help overcome this error. However, there are upper limits on these alternatives. There is a limit on the solubility of WF_5X in C_6F_6, although the value has not been determined. The counting tubes are a standard size and this limits the volume of reactants which can be studied. Several other aspects of the experimental procedure are worth comment. Two types of P.T.F.E. glass stop-cocks were used. The Fischer and Porter type, although more reliable, have a narrow bore. The Rotaflo stop-cock has a wide bore making it easier to introduce sample directly to the bottom of the tube using a pipette, but these stop-cocks are prone to leaks due to particles of dust trapped at the teflon-to-glass seal. These latter stop-cocks were used on the vacuum manifold used for transfer of Me_3Si^*F to and from the tungsten compound, and it is thought that discrepancies in the count rates observed in some of the experiments are due to loss of Me_3Si^*F due to poor vacuum.

Possible Application of These Techniques to I(V) Fluorides

The exchange reaction between WF_6 and Me_3SiF could not be studied in detail[191] as the reactants could not be efficiently separated by physical or chemical means. This problem does not exist with IF_5 and Me_3SiF as their volatilities are sufficiently different but IF_5 does react with Me_3SiF at 20°C making a detailed study of this exchange reaction impractical. The substitution derivatives of IF_5, for example IF_4OMe and IF_4OEt, do not readily react with Me_3SiF but lose HF at room temperature. This would complicate any study on fluorine exchange. However, IF_4OMe is the most stable of the alkoxo derivatives which have been prepared and it may be possible to obtain meaningful results by studying the IF_4OMe, $Me_3\overset{*}{S}iF$ system.

Of the perfluoroalkyl derivatives of IF_5 , CF_3IF_4 is probably too unstable but the more stable derivatives like $(CF_3)_2CFIF_4$ and $C_6F_5IF_4$ appear to be suitable candidates for such a study. The perfluorocarbon groups may also slowly exchange with the $Me_3\overset{*}{S}iF$ but the rate should be much slower than the exchange rate of the iodine fluorines. It would be interesting to look at the exchange in compounds of the type $SF_5(CF_2)_nIF_4$. The rate of exchange in this case would be expected to be, in decreasing order :

$$IF \gg SF > CF$$

Unfortunately the alkoxosubstituted derivatives of R_FIF_4 do not appear to be stable enough to study using the techniques described in this chapter. Different rates of exchange have been observed for the different types of iodine fluorines in R_FIF_3OMe and it would have been interesting to study these rates kinetically.

EXPERIMENTAL

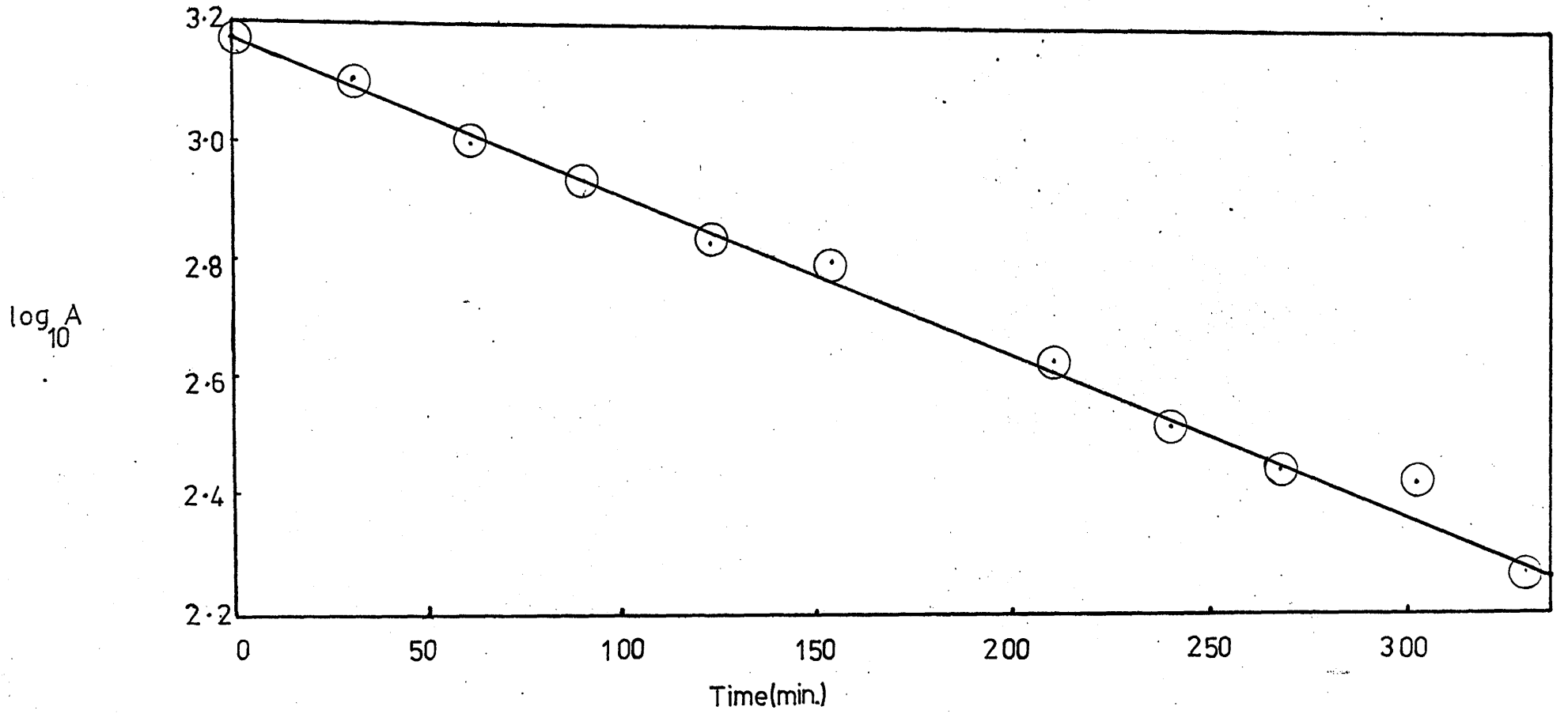
Standard vacuum techniques were used. Me_3SiF was produced in the reaction of WF_6 (Alfa Inorganics) with excess Me_3SiNEt_2 (B.D.H.). It was purified by fractional distillation and its purity confirmed by i.r., n.m.r. and mass spectrometry. WF_6 was purified by trap-to-trap distillation and stored over NaF. Me_3SiNEt_2, similarly purified was stored over Linde 4A molecular sieves. C_6F_6 (Imperial Smelting Co.) was purified by vacuum distillation and dried over sodium. WF_5OMe and WF_5OPh were prepared from the reaction of excess WF_6 with Me_3SiOMe or $(MeO)_2SO$ and Me_3SiOPh respectively. WF_5OMe and WF_5OPh were purified by removing the WF_6 and Me_3SiF or $MeOS(O)F$ at 20°C. The solutions of WF_5OR were handled in a Lintott inert atmosphere box in which the concentrations of H_2O and O_2 were $\leqslant$ 10 p.p.m.

Radioactivity Measurements

^{18}F activities were determined using a NaI well scintillation counter (Ekco Instruments), well dimensions $\frac{25}{16}$ x $\frac{35}{32}$ in diameter. Samples were contained in pyrex ampoules of uniform bore, 10 mm ($\sim$ 5 ml. volume), fitted with P.T.F.E.-glass stop-cocks (Fischer and Porter or Quickfit "Rotaflo"). Me_3SiF was counted in the liquid phase or in C_6F_6 solution. It was found that the counting efficiency of Me_3SiF was increased when it was in C_6F_6 solution. Tungsten compounds were hydrolysed and counted in acetone solution to improve counting efficiency over a solid state count. Reproducible counts were obtained in all cases.

Preparation of Labelled Me_3SiF

Fluorine-18 was prepared by neutron irradiation (1 h; flux =



Typical ^{18}F Decay Curve

Fig.10.

3×10^{12} $cm^{-2}s^{-1}$) of lithium carbonate (2 g, B.D.H. AnalaR) according to ^{6}Li (n, α)t; ^{16}O(t, n) ^{18}F in the Scottish Universities Research Reactor, East Kilbride. Aqueous solutions of $Cs^{18}F$ prepared according to the scheme :[194]

$$Li^{18}F \xrightarrow[\text{distil}]{50\%\ H_2SO_4} H^{18}F \xrightarrow[0^{\circ}C]{CsOH\ aq} Cs^{18}F\ aq.$$

The solution activities were typically 0.2 mCi. Neutralisation with 40% HF followed by evaporation and drying (1 h; i.r. lamp) gave solid $Cs^{18}F$ which was further dried <u>in vacuo</u>.

Me_3SiF was labelled by exchange with $Cs^{18}F$ in a stainless steel (75 ml.) pressure vessel (Hoke Ltd.) fitted with a Hoke needle valve and maintained at > 80°C for 45-60 min. The radiochemical purity of Me_3SiF was checked by decay curve determination over at least three half-lives. Calculated $t_{\frac{1}{2}}$ values agreed with the previously reported value of 110 min.[195] A typical decay curve is shown in Fig. 10. The half-life of ^{18}F calculated from the slope of the graph is 109.2 min.

<u>Exchange Reactions</u>

Labelled Me_3SiF was distilled onto a known weight of solution of predetermined concentration and its weight and activity measured. All exchange reactions were performed in a thermostatically controlled water bath at 26 $\pm$ 1°C for varying lengths of time (30 - 250 mins.). After exchange, the volatile fraction (Me_3SiF + C_6F_6) was removed between -196°C and 20°C and weighed to ensure complete separation. The activities of both fractions were measured and corrected for ^{18}F decay. The radiochemical balance was not always within 95% (see Tables 1-8) and this was thought to be due to loss of $Me_3Si^{*}F$ in the vacuum system.

APPENDIX

I. Mass Spectra of Perfluoroalkyl and aryl halides.

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		1. CF_3I			
196	100	CF_3I^+	127	66	I^+
177	29	CF_2I^+	69	86	CF_3^+
158	1	CFI^+	50	9	CF_2^+
146	3	IF^+	31	9	CF^+
139	2	CI^+			
		2. C_2F_5I			
246	100	$C_2F_5I^+$	100	35	$C_2F_4^+$
227	21	$C_2F_4I^+$	81	1	$C_2F_3^+$
208	1	$C_2F_3I^+$	69	79	CF_3^+
177	40	CF_2I^+	62	< 1	$C_2F_2^+$
158	8	CFI^+	50	15	CF_2^+
139	3	CI^+	43	< 1	C_2F^+
127	7	I^+	31	41	CF^+
119	83	$C_2F_5^+$			

Metastable Transitions

M_1	Transition	M_2	M^* obsd.	M^* calcd.
246	$C_2F_5I^+ \longrightarrow C_2F_5^+ + I^\cdot$	119	57.6	57.6
227	$C_2F_4I^+ \longrightarrow C_2F_4^+ + I^\cdot$	100	44.1	44.1

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		3. $(CF_3)_2CFI$			
296	100	$C_3F_7I^+$	131	19	$C_3F_5^+$
277	13	$C_3F_6I^+$	127	61	I^+
258	1	$C_3F_5I^+$	119	7	$C_2F_5^+$
239	< 1	$C_3F_4I^+$	112	2	$C_3F_4^+$
227	5	$C_2F_4I^+$	100	37	$C_2F_4^+$
208	2	$C_2F_3I^+$	93	3	$C_3F_3^+$
189	1	$C_2F_2I^+$	81	27	$C_2F_3^+$
177	29	CF_2I^+	74	1	$C_3F_2^+$
169	12	$C_3F_7^+$	69	94	CF_3^+
158	3	CFI^+	62	1	$C_2F_2^+$
150	20	$C_3F_6^+$	50	3	CF_2^+
146	1	IF^+	43	< 1	C_2F^+
139	1	CI^+	31	25	CF^+

Metastable Transitions

M	Transition	M_2	M^* obsd.	M^* calcd.
277	$C_3F_6I^+ \longrightarrow CF_2I^+ + C_2F_4^\cdot$	177	113.0	113.1
277	$C_3F_6I^+ \longrightarrow C_3F_5 + IF^\cdot$	131	62.0	61.95
169	$C_3F_7 \longrightarrow CF_3^+ + C_2F_4^\cdot$	69	28.3	28.2

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		4. n - C_4F_9I			
346	28	$C_4F_9I^+$	146	< 1	IF^+
327	1	$C_4F_8I^+$	139	1	CI^+
246	2	$C_2F_5I^+$	131	29	$C_3F_5^+$
239	4	$C_3F_4I^+$	127	40	I^+
227	2	$C_2F_4I^+$	119	22	$C_2F_5^+$
220	2	$C_3F_3I^+$	112	2	$C_3F_4^+$
219	45	$C_4F_9^+$	100	26	$C_2F_4^+$
208	4	$C_2F_3I^+$	93	7	$C_3F_3^+$
200	< 1	$C_4F_8^+$	81	3	$C_2F_3^+$
189	< 1	$C_2F_2I^+$	74	2	$C_3F_2^+$
182	< 1	C_3FI^+	69	100	CF_3^+
131	8	$C_4F_7^+$	62	2	$C_2F_2^+$
177	22	CF_2I^+	55	1	C_3F^+
169	3	$C_3F_7^+$	50	4	CF_2^+
158	3	CFI^+	36	1	C_3^+
150	3	$C_3F_6^+$	31	23	CF^+

Metastable Transitions

M_1	Transition	M_2	M^* obsd.	M^* calcd.
346	$C_4F_9I^+ \longrightarrow C_4F_9^+ + I^\cdot$	219	138.8	138.8
219	$C_4F_9^+ \longrightarrow C_3F_7^+ + CF_2^\cdot$	131	78.2	78.2

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		5. ICF_2CF_2I			
354	17	$C_2F_4I^+$	100	57	$C_2F_4^+$
254	16	I_2^+	81	80	$C_2F_3^+$
227	19	$C_2F_4I^+$	77	3	unassigned
224	3	unassigned	69	63	CF_3^+
208	6	$C_2F_3I^+$	62	2	$C_2F_2^+$
177	8	CF_2I^+	80	28	CF_2^+
158	4	CFI^+	44	100	CO_2^+
139	1	CI^+	43	2	C_2F^+
127	22	I^+	31	91	CF^+

Metastable Transitions

M_1	Transition	M_2	M^* obsd.	M^* calcd.
354	$C_2F_4I_2^+ \longrightarrow I_2^+ + C_2F_4^{\cdot}$	254	182.1	182.1

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		6. C_6F_5I			
294	100	$C_6F_5I^+$	110	2	$C_6F_2^+$
275	2	$C_6F_4I^+$	98	16	$C_5F_2^+$
225	< 1	$C_5F_2I^+$	93	16	$C_3F_3^+$
167	50	$C_6F_5^+$	86	4	$C_4F_2^+$
148	11	$C_6F_4^+$	79	12	C_5F^+
147	7	$C_6F_5I^{+}_{2e}$	74	2	$C_3F_2^+$
136	1	$C_5F_4^+$	60	1	C_5^+
129	2	$C_6F_3^+$	55	2	C_3F^+
127	14	I^+	43	1	C_2F^+
117	62	$C_5F_3^+$	31	15	CF^+

Metastable Transitions

M_1	Transition	M_2	M^* obsd.	calcd.
294	$C_6F_5I^+ \longrightarrow C_6F_5^+ + I^\cdot$	167	94.9	95.0
167	$C_6F_5^+ \longrightarrow C_5F_3^+ + CF_2^\cdot$	117	82.0	82.0

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		8. C_6F_5Br.			
a.					
246	96	$C_6F_5{}^{79}Br^+$	110	3	$C_6F_2^+$
227	3	$C_6F_4Br^+$	105	4	$C_4F_3^+$
215	2	$C_6F_4Br^+$	98	29	$C_5F_2^+$
177	2	$C_5F_2Br^+$	93	23	$C_3F_3^+$
167	81	$C_6F_5^+$	86	8	$C_4F_2^+$
158	1	$^{79}Br_2^+$	79	22	$^{79}Br^+$, C_5F^+
148	15	$C_6F_4^+$	74	10	$C_2F_3^+$
123	6	$C_6F_5{}^{79}Br$	69	4	CF_3^+
117	100	$C_5F_3^+$	55	6	C_3F^+
			31	31	CF^+

Metastable Transitions

M_1	Transition	M_2	M^* obsd.	M^* calcd.
246	$C_6F_5{}^{79}Br^+ \longrightarrow C_6F_5^+ + {}^{79}Br^\cdot$		113.4	113.4
248	$C_6F_5{}^{81}Br^+ \longrightarrow C_6F_5^+ + {}^{81}Br^\cdot$		112.5	112.5
167	$C_6F_5^+ \longrightarrow C_5F_3 + CF_2^\cdot$		82.0	82.0

a. ions correspond to ^{79}Br. throughout. The expected isotope patterns are observed in each case.

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		7. $C_6F_4I_2$			
402	94	$C_6F_4I_2^+$	98	95	$C_5F_2^+$
275	27	$C_6F_4I^+$	93	5	$C_3F_3^+$
256	2	$C_6F_3I^+$	91	2	C_6F^+
254	15	I_2^+	86	4	$C_4F_2^+$
225	2	$C_5F_2I^+$	79	36	C_5F^+
201	7	$C_3F_2I^+$	74	9	$C_3F_2^+$
148	100	$C_6F_4^+$	69	0.5	CF_3^+
139	1	CI^+	67	1	C_4F^+
129	15	$C_6F_3^+$	60	2	C_5^+
127	36	I^+	55	2	C_3F^+
117	20	$C_5F_3^+$	50	0.5	CF_2^+
110	8	$C_6F_2^+$	31	21	CF^+

Metastable Transitions

m_1	Transition	m_2	m^* obsd.	m^* calcd.
402	$C_6F_4I_2^+ \longrightarrow C_6F_4I^+ + I^\cdot$	275	188.0	188.1
148	$C_6F_4^+ \longrightarrow C_5F_3^+ + CF^\cdot$	117	92.6	92.5
275	$C_6F_4I^+ \longrightarrow C_6F_4^+ + I^\cdot$	148	79.8	79.7
256	$C_6F_3I^+ \longrightarrow C_6F_3^+ + I^\cdot$	129	~65.0	65.0
148	$C_6F_4^+ \longrightarrow C_5F_2^+ + CF_2^\cdot$	98		64.9
198	$C_5F_2^+ \longrightarrow C_5F^+ + F^\cdot$	79	63.7	63.7
79	$C_5F^+ \longrightarrow C_4F^+ + C^\cdot$	67	56.8	56.8
402	$C_6F_4I_2^+ \longrightarrow C_6F_4^+ + I_2^\cdot$	148	54.6	54.5

II Mass Spectra of Iodoperfluoroalkylsulphur(VI) Pentafluoride.

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
		1. $SF_5CF_2CF_2I$			
a.					
354	9	$C_2F_9IS^+$	101	3	CF_3S^+
246	2	$C_2F_{10}S^+$, $C_2F_5I^+$	100	86	$C_2F_4^+$
227	70	$C_2F_9S^+$, $C_2F_4I^+$	89	70	SF_3^+
208	8	$C_2F_8S^+$, $C_2F_3I^+$	82	1	CF_2S^+
177	16	CF_7S^+, CF_2I^+	81	9	$C_2F_3^+$
170	1	$C_2F_6S^+$, C_2FI^+	70	24	SF_2^+
158	8	CF_6S^+, CFI^+	69	49	CF_3^+
146	1	IF^+	63	4	CFS^+
139	2	CF_5S^+, CI^+	62	15	$C_2F_2^+$
131	1	$C_3F_5^+$	51	7	FS^+
127	78	F_5S^+, I^+	50	14	CF_2^+
120	2	CF_4S^+	44	2	CS^+
119	100	$C_2F_5^+$	43	1	C_2F^+
108	1	SF_4^+	31	45	CF^+
105	1	$C_4F_3^+$			

Metastable transitions

M_1	Transition	M_2	M^* obsd.	M^* calcd.
354	$C_2F_9IS^+ \longrightarrow C_2F_9S^+ + I^\cdot$	246		
	$C_2F_9IS^+ \xrightarrow{\text{or}} C_2F_5I^+ + SF_5^\cdot$	246	170–171	170.9
227	$C_2F_4I^+ \longrightarrow C_2F_4^+ + I^\cdot$	100	44.1	44.1
	$C_2F_9S^+ \xrightarrow{\text{or}} C_2F_4^+ + SF_5^\cdot$	100		
354	$C_2F_9IS^+ \longrightarrow C_2FS^+ + SF_4I^\cdot$	119	40.0	40.0

2. $SF_5CF_2CF_2CF_2CF_2I$

a.

m/e	Relative Abundance	Assignment	m/e	Relative Abundance	Assignment
454	10	$C_4F_{13}IS^+$	132	1	$C_2F_4S^+$
327	8	$C_4F_{13}S^+, C_4F_8I^+$	131	14	$C_3F_5^+$
277	1	$C_3F_{11}S^+, C_3F_6I^+$	127	46	SF_5^+, I^+
254	1	I_2^+	119	23	$C_2F_5^+$
239	6	$C_3F_9S^+, C_3F_4I^+$	112	2	$C_3F_4^+$
227	4	$C_2F_9S^+, C_2F_4I^+$	108	0.4	SF_4^+
220	1	$C_3F_8S^+, C_3F_3I^+$	100	46	$C_2F_4^+$
219	37	$C_4F_9^+$	93	6	$C_3F_3^+$
208	6	$C_2F_8S^+, C_2F_3I^+$	89	37	SF_3^+
200	1	$C_4F_8^+$	81	4	$C_2F_3^+$
189	0.5	$C_2F_7S^+, C_2F_2I^+$	74	1	$C_3F_2^+$
182	1	$C_3F_6S^+, C_3FI^+$	70	5	SF_2^+
181	20	$C_4F_7^+$	69	100	CF_3^+
177	23	CF_7S^+, CF_2I^+	62	1	$C_2F_2^+$
169	1	$C_3F_7^+$	51	1	SF^+
158	2	CF_6S^+, CFI^+	50	4	CF_2^+
150	1	$C_3F_6^+$	31	17	CF^+

Metastable Transitions

M_1	Transition	M_2	M^* obsd.	M^* calcd.
327	$C_4F_{13}S^+ \rightarrow C_3F_9S^+ + CF_4^\cdot$ or $C_4F_8I^+ \rightarrow C_3F_4I^+ + CF_4^\cdot$	239	174.5	174.6
454	$C_4F_{13}IS^+ \rightarrow C_4F_9^+ + SF_4I^\cdot$	219	105.7	105.6
327	$C_4F_{13}S^+ \rightarrow C_4F_7^+ + SF_6^\cdot$ or $C_4F_8I^+ \rightarrow C_4F_7^+ + IF^\cdot$	181	100.1	100.2
219	$C_4F_9^+ \rightarrow C_3F_7^+ + CF_2^\cdot$	131	78-79	78.4
181	$C_4F_7^+ \rightarrow C_2F_5^+ + C_2F_2^\cdot$	119		78.2

M_1	Transition	M_2	M^* obsd.	calcd.
181	$C_4F_7^+ \longrightarrow C_3F_3^+ + CF_4^{\cdot}$	93	47.8	47.8
132	$CF_4S^+ \longrightarrow SF_2^+ + CF_2^{\cdot}$	70	37.2	37.1

a ions correspond to ^{32}S. The expected isotope patterns are observed.

III Mass Spectrum of IF_5

$m/_e$	Relative Abundance	Assignment
254	64	I_2^+
222	9	IF_5^+
203	100	IF_4^+
184	23	IF_3^+
165	7	IF_2^+
146	7	IF^+
127	28	I^+
82.5	6	$165/_{2e}$

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